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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXIII. A Synthesis of Kellin*

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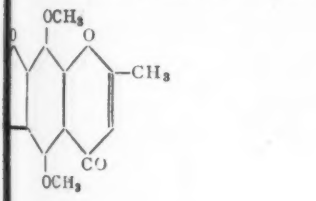
Received May 30, 1949

Kellin is the most important chemical component of the fruits of *Ammi Visnaga*, a plant belonging to the family Umbelliferæ. It is found in Egypt and the neighbouring Mediterranean countries. The crude drug has been used for a long time as a cure for leucoderma. Recently, Kellin has been found to be very useful in the treatment of spasmodic conditions like asthma and intestinal colic and also for certain diseased conditions of the heart. Its constitution was established by Späth and Gruber[1] as 2-methyl-5: 8-dimethoxy-7: 6-furano-chromone (I). For working out its synthesis, two ways are possible: (1) building up the furan ring on the required chromone system, and (2) building up the pyrone ring on the appropriate coumarone. Both these were examined in the case of the synthesis of karanjin[2]; the latter was found to be eventually successful. In a recent publication Robertson



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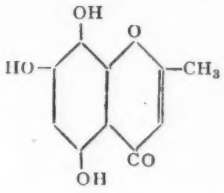

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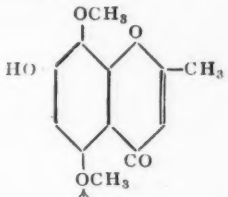

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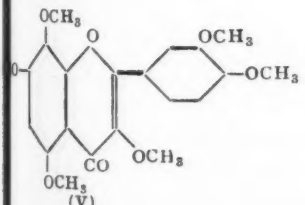

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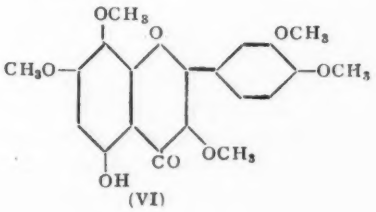

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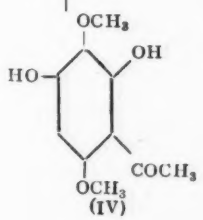
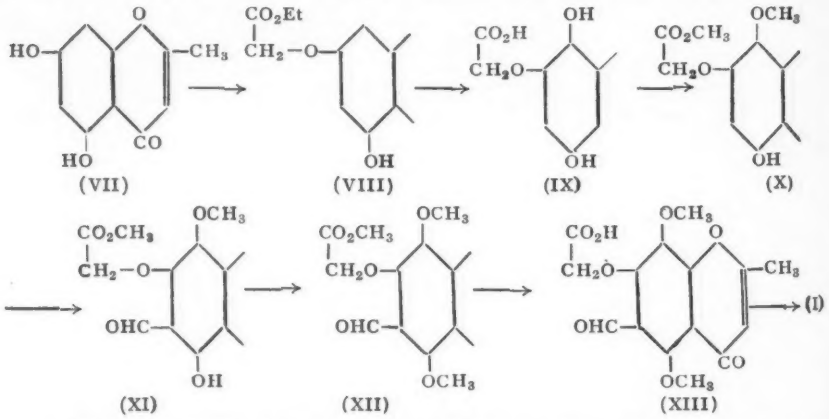


(IV)

* A preliminary note was submitted to the Editor, *J.S.I.R.*, on 25—4—1949.

and co-workers[3] also have expressed the opinion that the second procedure is the more feasible of the two, particularly for the synthesis of the linear furano-chromones. But in the course of our recent work on nuclear oxidation in flavones and related compounds, there were indications that method I could be successful in the synthesis of kellin.

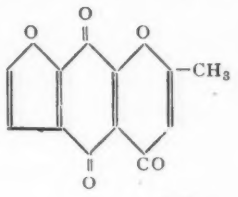
From the structure of kellin as given by Späth and Gruber, it is a derivative of 2-methyl-5: 7 : 8-trihydroxy chromone (II). The 5: 8-dimethyl-ether of this compound (III) could be directly made from 2 : 4-dihydroxy-3: 6-dimethoxy acetophenone (IV) which is known.[4] If an aldehydo group could be put into the 6-position of the ether (III) the synthesis of kellin could be readily achieved. But exploratory experiments[5] using the more readily available gossypetin pentamethyl ether with the 7-hydroxyl free (V) showed that the 6-position was not reactive. On the other hand, the isomeric 5-hydroxy compound (VI) reacted readily. It was, therefore, concluded that a free hydroxyl in the 5-position is necessary for the success of the synthesis. The procedure described below is based on these considerations and also conveniently utilizes alkaline persulphate oxidation which has been extremely successful for the (para) nuclear oxidation of flavones.



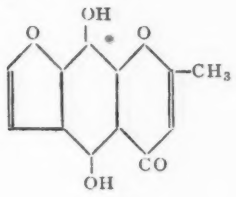
2-Methyl-5: 7-dihydroxy-chromone (VII)[6] is the starting point and its preparation has been effected by a modified process giving rise to improved yields. It is condensed with one mole of bromacetic ester using anhydrous potassium carbonate in acetone medium. The reactive hydroxyl in the 7-position takes part. The resulting phenoxy-acetic ester (VIII) is subjected to para-oxidation with alkaline persulphate. This introduces a hydroxyl in the 8-position (*cf.* oxidation of tectochrysin[7]) and at the same time the ester group undergoes hydrolysis yielding the dihydroxy acid (IX). This acid

is rather too unstable to be used directly for aldehyde synthesis. Methylation using two moles of dimethyl sulphate in acetone in the presence of potassium carbonate converts it into the 8-methoxy-phenoxy acetic ester (X) the resistant 5-hydroxyl being left out. This compound undergoes condensation with hexamine in glacial acetic acid solution yielding the 6-aldehyde (XI). Final methylation with excess of dimethyl sulphate gives the dimethoxy aldehydo-ester (XII). Gentle hydrolysis with alkali provides the required carboxylic acid (XIII) which when boiled with acetic anhydride and sodium acetate forms the furan ring with the simultaneous evolution of carbon dioxide. The product (I) melts at 154-55° and has the same crystal form as natural kellin. Previous workers[1] have recorded that it crystallises as colourless needles but it is now noted that on slow crystallisation it comes out as stout rectangular prisms though rapid crystallisation produces needles. The mixture of the natural and synthetic products does not exhibit any depression in melting point.

For a more thorough comparison of the natural and synthetic samples a readily available derivative was needed. This has been found in the oxidation of kellin with nitric acid whereby oxidative demethylation[1,8] takes place yielding the orange-yellow quinone (XIV). This melts at 215–16° with decomposition and has been used for comparison. The natural and synthetic samples are found to be identical. Further, reduction of the quinone with sulphur dioxide in alcoholic solution yields the corresponding quinol (XV) melting at 285–87° with decomposition. That this is the correct nor-kellin is proved by methylating it to kellin.



(XIV)



(XV)

Experimental

5 : 7-*Dihydroxy*-2-*methyl chromone* (*VII*)

This substance was prepared earlier by Joachum and Kostanecki and also by Gulati, Seth and Venkataraman.[6] The following modified procedure gives rise to better yields of a purer product.

Dry phloracetophenone (6 g.) was dissolved in acetic anhydride (25 c.c.) and freshly fused sodium acetate (10 g.) added. The mixture was

gently refluxed in an oil-bath for 6 hours. The dark brown mixture was cooled in ice-water and the acetic anhydride was decomposed by the addition of alcohol. After the reaction was over the contents were left overnight; the ethyl acetate that was formed was then removed under reduced pressure and the residue treated with water when the chromone acetate gradually separated as a pale-brown crystalline solid. This was filtered, washed with water, suspended in 5% aqueous alcoholic sodium carbonate solution (50 c.c.) and gently refluxed for one hour. The solution was filtered from suspended impurities, and acidified with dilute hydrochloric acid while cooling in ice-water. The chromone was precipitated as a pale yellow solid. It crystallised from alcohol-ethyl acetate mixture as very pale yellow stout prisms melting at 279–80°. Yield, 2·5 gm.

5-*Hydroxy*-7-O-*carbethoxymethyl*-2-*methyl-chromone* (*VIII*)

The dihydroxy chromone (2·4 g.) was dissolved in dry acetone (200 c.c.) and freshly ignited potassium carbonate (10 g.) and ethyl bromo-acetate (2·0 c.c.) were added and the mixture refluxed for 8 hours. The acetone solution was filtered, the solvent removed by distillation and the product crystallised from alcohol-petroleum ether mixture when it was obtained as colourless tiny prisms melting at 123–4°. It gave a violet-red ferric chloride colour turning brown-red with excess of the reagent and showed a weak green fluorescence in alcoholic solution. Yield, 1·5 g. (Found: C, 60·7; H, 5·3; $C_{14}H_{14}O_6$ requires C, 60·4; and H, 5·0%.)

5: 8-*Dihydroxy*-7-O-*carboxymethyl*-2-*methyl chromone* (*IX*)

The above compound (VIII) (1·0 g.) was dissolved in aqueous sodium hydroxide (2 g. in 50 c.c. of water) and a solution of potassium persulphate (3 g. in 50 c.c. of water) added slowly in 4 hours. During the addition the contents were cooled in ice-water and mechanically stirred. The red solution was allowed to stand overnight, then acidified to congo-red with hydrochloric acid and filtered from a small amount of fluffy matter that separated out. After an extraction with ether a further quantity (15 c.c.) of concentrated hydrochloric acid and sodium sulphite (5 g.) were added and the mixture heated on a boiling water-bath for half an hour. On cooling, a yellow powder separated which was filtered, washed free from acid and crystallised from alcohol-ether mixture when the quinol-acid (IX) was obtained as yellow rectangular prisms. The compound darkens at 220° and melts with decomposition at 229°-31°. It dissolves in 5% aqueous sodium carbonate to give a yellow solution; the colour gradually changes to pink-brown and fades. With ferric chloride in alcoholic solution, the compound gives a bluish-green colour changing to green with excess and

finally turning red; a dark brown precipitate separates on standing. (Found: C, 54·4; H, 3·9; $C_{12}H_{10}O_7$ requires C, 54·1 and H, 3·8%.)

5-Hydroxy-8-methoxy-7-O-carbomethoxymethyl-2-methyl chromone (*X*)

The dihydroxy-acid (IX) (0·5 g.) was methylated in dry acetone solution (30 c.c.) with freshly distilled dimethyl sulphate (0·4 c.c., 2 moles) in the presence of potassium carbonate (5 g.) by refluxing for 6 hours. The product crystallised from methyl alcohol as colourless needles melting at 137–8° and gave a pink-brown ferric chloride colour. Yield, 0·3 g. (Found: C, 56·9; H, 5·0; $C_{14}H_{14}O_7$ requires C, 57·1 and H, 4·8%.)

5-Hydroxy-8-methoxy-7-O-carbomethoxymethyl-2-methyl-chromone-6-aldehyde (*XI*)

The above ether-ester (X) (0·6 g.) was dissolved in glacial acetic acid (20 c.c.), hexamine (2 g.) added and the mixture heated in a boiling water-bath for 6 hours. A mixture of fuming hydrochloric acid and water (1 : 1; 10 c.c.) was then added and heating continued for half an hour more. The reaction mixture was diluted with water, neutralized with sodium bicarbonate and extracted with a large volume of ether. On distilling off the ether, the aldehyde was obtained as a yellow solid. It crystallised from rectified spirit as yellow flat needles and narrow rectangular plates melting at 149–50°. It gave a brown colour with ferric chloride in alcoholic solution. Yield, 0·1 g. (Found: C, 56·2; H, 4·7; $C_{15}H_{14}O_8$ requires C, 55·9 and H, 4·4%.)

5:8-*Dimethoxy-7-O-carbomethoxymethyl-2-methylchromone-6-aldehyde* (*XII*)

The hydroxy-aldehyde (XI) (0·3 g.) was completely methylated in acetone solution (25 c.c.) with dimethyl sulphate (0·2 c.c.) and potassium carbonate (5 g.) by refluxing for 30 hours. The product crystallised from alcohol as colourless prismatic needles melting at 142–3°. Yield, 0·2 g. (Found: C, 57·4; H, 5·1; $C_{16}H_{16}O_8$ requires C, 57·2 and H, 4·8%.)

2-Methyl-5: 8-*dimethoxy-7-O-carboxymethyl-chromone-6-aldehyde* (*XIII*)

The methyl ester (0·5 g.) was suspended in 2% potassium hydroxide (10 c.c.) and heated on a water-bath for 10 minutes. The solution was filtered, cooled in ice-water, acidified with dilute hydrochloric acid and extracted with a large volume of ether. The ether extract was dried over anhydrous sodium sulphate and the solvent distilled off. A viscous oil was left behind and it solidified on cooling. It crystallised from methyl alcohol as small colourless prisms melting at 179–80°. Yield, 0·3 g. (Found: C, 56·2; H, 4·6; $C_{15}H_{14}O_8$ requires C, 55·9; and H, 4·4%.)

Kellin (I)

The above aldehydo-acid (XIII) (0·2 g.) was dissolved in acetic anhydride (5 c.c.), fused sodium acetate (2 g.) added and the mixture gently refluxed in an oil-bath for 2 hours. It was then treated with ice-water, neutralized with sodium bicarbonate and the product extracted with ether. Some amount of sparingly soluble resinous matter was filtered off. The ether extract was washed with 5% sodium bicarbonate solution and water and the solvent evaporated. A pale yellow solid remained behind which on crystallisation from methyl alcohol appeared as thick, long, rectangular prisms melting at 154–55°. The mixed melting point with a sample of natural kellin was undepressed. Yield, 50 mg. (Found: C, 64·9; H, 4·8; $C_{14}H_{12}O_5$ requires C, 64·6 and H, 4·6%.)

Nitric acid oxidation of kellin to kellin-quinone (XIV)

Kellin (0·5 g.) was treated with nitric acid (d., 1·2; 5 c.c.) while cooling in ice and stirring with a glass rod. The substance dissolved with a deep red colour and immediately the quinone separated as an orange solid. After 15 minutes, water was added, the solid product filtered and washed free from acid and crystallised from alcohol in which it was moderately soluble. The quinone (XV) separated as orange-yellow needles and narrow rectangular prisms melting at 215–16° with decomposition. It was identical in all respects with a sample of the quinone obtained from natural kellin. (Found: C, 63·0; H, 2·9; $C_{12}H_6O_5$ requires C, 62·6 and H, 2·6%.)

Reduction to nor-kellin (XV)

Kellin-quinone (0·2 g.) was suspended in alcohol (20 c.c.) and sulphur dioxide was passed for half an hour. The quinone went into solution which gradually assumed a yellow colour. When concentrated the quinol came out as a crystalline solid. Further recrystallisation from alcohol yielded stout yellow rectangular prisms melting at 285–87° with decomposition. It gave a deep green colour with alcoholic ferric chloride, changing to red with excess. With *p*-benzoquinone in alcoholic solution, it produced a deep-red colour. (Found: C, 62·5; H, 3·8; $C_{12}H_8O_5$ requires C, 62·1; and H, 3·5%). Methylation with excess of dimethyl sulphate and potassium carbonate in dry acetone medium regenerated kellin.

SUMMARY

Kellin (I) has been synthesised starting from 2-methyl-5: 7-dihydroxychromone (VII). The stages are as follows: (1) treatment with bromacetic ester (VIII); (2) oxidation with alkaline persulphate in which the ester group gets hydrolysed (IX); (3) partial methylation with 2 moles of dimethyl

sulphate (X); (4) condensation with hexamine to introduce an aldehyde group in the 6-position (XI); (5) complete methylation (XII); (6) gentle alkali hydrolysis to aldehydo-acid (XIII); and (7) final boiling with acetic anhydride and sodium acetate. Kellin-quinone and nor-kellin have been prepared as convenient derivatives.

We are further employing this method for the synthesis of the isomers and analogues of kellin.

Our thanks are due to Professors A. Schönberg and R. B. Fahmy of Cairo for samples of natural kellin.

Note added in Proof.—After submitting this paper for publication we received the issue of the *J.C.S.* containing the paper of Clarke and Robertson on the " Synthesis of Kellin and related Compounds (1949, 302) " Their method is different from ours. Following earlier work in this line they have first prepared kellinone, an ortho-hydroxy ketone having the coumarone ring system and subsequently built up the *r*-pyrone part to get kellin. By the ordinary method of demethylation using hydriodic acid they did not succeed in obtaining nor-kellin since the reaction was accompanied by isomeric change.

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8. ———— .. *Ibid.*, 1948, **27**, 245.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXIV. Synthesis of Myristicin and Elemicin

By K. Visweswara Rao, T. R. Seshadri, F.A.Sc., and T. R. Thiruvengadam

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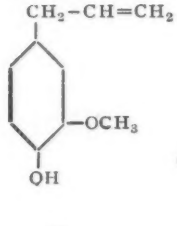
Received June 13, 1949

In some of the previous parts[1] experiments using flavones were described in support of the mechanism of phytochemical ortho-oxidation that it takes place in multiple stages. The work is now extended to simpler benzene derivatives which have biogenetic analogy. Eugenol (I) is a fundamentally important compound occurring in nature. It has the allyl-catechol unit which may be considered to arise in the same way as the nine carbon system comprising the side phenyl nucleus and pyrone carbon atoms of flavones (see Robinson[2]). Myristicin (II)[3] present in nutmeg, mace and parsley and elemicin (III)[4], a component of elemi oil, are derivatives of allyl pyrogallol and may be considered to be related to eugenol just in the same way as myricetin is derived from quercetin and robinetin from fisetin by processes involving ortho-oxidation. These considerations have led to a simple and elegant method of synthesis of these compounds (II and III) which is the subject-matter of the present communication. The suitability of this method of ortho-oxidation for preparing methylene-dioxy compounds has already been illustrated using the example of kanugin.[1]



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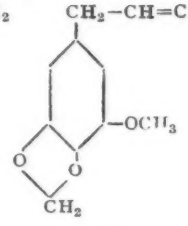

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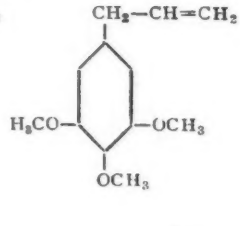
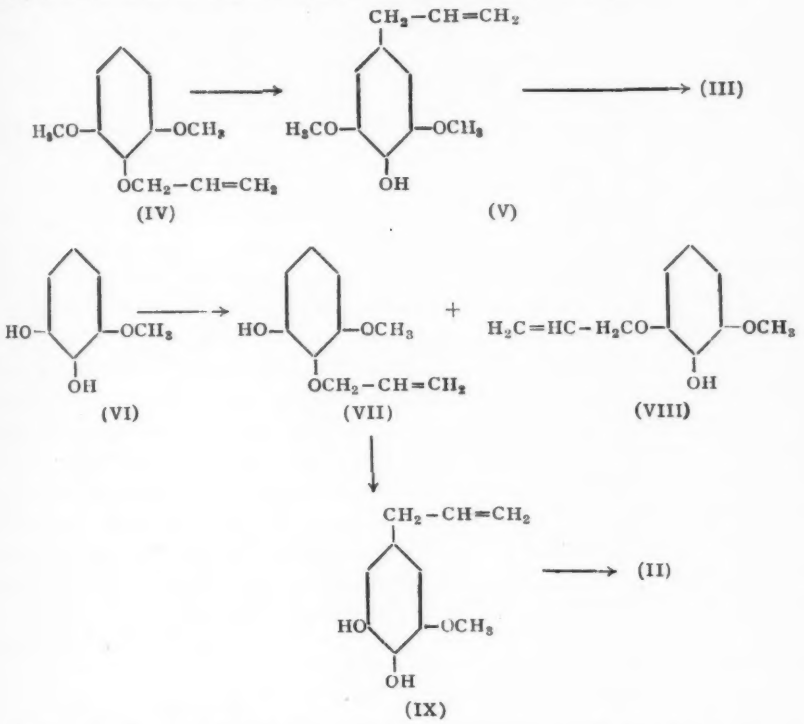


(III)

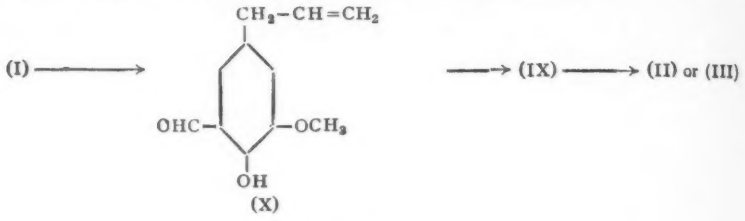
Originally Mauthner[5] synthesised elemicin by subjecting 1 : 3-dimethyl-2-allyl pyrogallol (IV) to allyl migration and methylating the resulting hydroxy compound (V). Regarding myristicin Trikojus and White[6] outlined in a preliminary note its synthesis from 1-methyl pyrogallol (VI). It gave a

mixture of two liquid monoallyl ethers (VII and VIII). They were separated and characterised as their 3:5-dinitrobenzoates. (VII) Rearranged on pyrolysis to give 3-methoxy-4:5-dihydroxy allyl benzene (IX) which was methylenated with methylene iodide to give myristicin (II).



Eugenol is now found to react with hexamine and give rise to a good yield of eugenol-5-aldehyde (X). This is a crystalline solid and exhibits the properties of an ortho-hydroxy aldehyde, forming a dinitrophenyl hydrazone and a sparingly soluble sodium salt and giving a deep blue colour with ferric chloride. In these reactions it resembles very closely orthovanillin. Its oxidation with hydrogen peroxide produces the corresponding catechol, 5-hydroxy-eugenol (IX). This is a viscous liquid, giving a green colour with ferric chloride and a yellow precipitate with lead acetate. It yields a colourless solid dibenzoate. Methylenation is carried out using methylene bromide and potassium carbonate in dry acetone medium. The product is a liquid whose identity with myristicin (II) is established by a study of its properties and also by preparing the solid dibromomyristicin dibromide. Similarly methylation

of the catechol (IX) using dimethyl sulphate yields elemicin (III). For establishing the identity of the product, besides its properties, is employed isomerisation with alkali and subsequent oxidation with permanganate yielding trimethyl gallic acid. It is interesting to note that all the stages in the above synthesis take place without noticeable isomerisation of the allyl side chain. (See Fodor[7] for benzylation of eugenol without isomerisation).



(X)

Experimental

Eugenol-5-aldehyde (X)

A solution of eugenol (10 c.c.) in glacial acetic acid (75 c.c.) was treated with hexamine (40 g.). The mixture was heated with shaking over a wire gauze to get a clear solution (pale brown) and was then kept in a boiling water-bath for six hours. The dark brown-red solution was treated while hot with a boiling mixture of concentrated hydrochloric acid (50 c.c.) and water (100 c.c.). Heating on the water-bath was continued for another five minutes and the mixture slowly cooled. It was extracted twice with ether and the ether extract washed with water. The clear ether solution was then shaken with 20% sodium hydroxide, added cautiously in small lots of 20 to 30 c.c. On shaking, the lower aqueous layer was colourless showing that only acetic acid had been extracted. Two or three such extractions removed all the acetic acid. Further addition of the alkali solution gave a bright yellow crystalline solid. After shaking vigorously the layers were allowed to separate and the lower layer diluted further with 10% alkali in order to complete the precipitation of the yellow sodium salt of eugenol-5-aldehyde. It was filtered and washed with 10% alkali and ether. It was then dissolved in excess of water and filtered and the clear filtrate acidified. After leaving overnight the pale cream coloured solid that separated out was filtered, washed well with water and dried. Yield, 3 g.

The alkaline filtrate from the sodium salt was acidified and extracted with ether. The ether extract was washed with water, concentrated to a small bulk and shaken thoroughly with strong aqueous sodium bisulphite. The crystalline bisulphite addition compound was filtered and washed with ether. It was treated with dilute sulphuric acid and the mixture heated in

a boiling water-bath till the solid disappeared giving oily drops. The mixture was cooled in the ice chest and the aldehyde that crystallised out was filtered. Yield, 1 g.

The aldehyde samples thus obtained melted at 51–2°; when recrystallised from petroleum ether it was obtained in the form of pale yellow prisms melting at 53–54°. It was also purified by distillation under reduced pressure (20 mm.), the fraction distilling at 148–50° being collected. On cooling in ice and scratching the sides of the tube, it rapidly solidified to give a mass of very pale yellow stout prisms melting at 53–4°. It was easily soluble in common organic solvents but sparingly in cold ligroin. In 10% sodium hydroxide it readily dissolved and the solution soon deposited yellow crystals of the sodium salt. With a drop of ferric chloride in alcoholic solution it gave a deep blue colour which did not change on further addition. (Found: C, 68·5; H, 6·6; $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·3%.)

Dinitrophenyl-hydrazone of Eugenol-5-aldehyde

An alcoholic solution of the aldehyde (0·2 g.) was treated with dinitrophenyl-hydrazine (0·2 g.) in alcohol (10 c.c.) and a few drops of concentrated hydrochloric acid. A copious crystalline precipitate of the dinitrophenyl-hydrazone was formed which was filtered after boiling for a few minutes. It was washed with alcohol and crystallised from ethyl acetate from which it separated as glistening orange red broad rectangular plates melting at 229–30°. (Found: C, 54·4; H, 4·4; $C_{17}H_{16}O_6N_4$ requires C, 54·8; H, 4·3%.)

5-*Hydroxy-eugenol* (*IX*)

To a solution of eugenol-5-aldehyde (2·5 g.) in pyridine (16 c.c.) was added one normal aqueous sodium hydroxide (19·5 c.c.) and the clear yellow solution treated dropwise with 6% hydrogen peroxide (9·6 c.c.) with vigorous shaking. The colour changed to red and when the solution developed turbidity a little more water was added in order to remove it. After leaving at the room temperature for 1½ hours with occasional shaking, the solution was acidified with hydrochloric acid while cooling. The hydroxy compound separated as a heavy liquid; this separation was completed by adding common salt and the mixture was extracted thrice with ether. The ether extract was washed successively with hydrochloric acid, aqueous sodium bicarbonate and a small quantity of water. After drying over sodium sulphate it was evaporated to remove the solvent completely; a pale brown viscous oil was left behind (2·0 g.). The product from three experiments was collected and distilled under reduced pressure (20 mm.); the main fraction distilled at 176°.

5-Hydroxy eugenol was a colourless viscous liquid. It was soluble in 5% aqueous sodium hydroxide and 10% aqueous sodium carbonate to give a deep brown solution. With a drop of ferric chloride in alcoholic solution it gave a deep violet colour changing to brownish violet and brown with another drop. After standing for a few minutes the colour changed to a stable olive green. It gave a yellow precipitate with lead acetate. (Found: C, 67·0; H, 6·4; $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%.)

Benzoylation: *Dibenzoate of 5-hydroxy eugenol*

The above dihydroxy compound was benzoylated by the Schotten-Baumann method. The benzoate separated from the alkaline solution in the form of a white sticky solid. It was extracted with ether, shaken well with 5% aqueous sodium hydroxide followed by water and dried over calcium chloride. On distilling off the ether a viscous liquid resulted which soon became an almost colourless crystalline solid. It was recrystallised from a mixture of ether and light petroleum from which it separated as colourless short rectangular prisms melting at 110–12°. (Found: C, 74·4; H, 5·2; $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·2%.)

Methylenation : Myristicin (II)

The dihydroxy compound (6 g.) was dissolved in anhydrous acetone (200 c.c.), treated with methylene bromide (7·5 c.c.) and potassium carbonate (30 g.) and refluxed for twenty hours. The solvent was then distilled off, the residue treated with water and the mixture extracted with ether. The ether extract was shaken with aqueous alkali, washed with water, dried over calcium chloride and distilled. The pale yellow oil left behind was distilled under reduced pressure (10 mm.) when myristicin passed over at 138°. Yield, 2 g. Its refractive index was 1·5368 at 31° for white light, and 1·5343 at 30° and 1·5412 at 20° for the D line. (Found: C, 68·6; H, 6·6; $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·3%.) When treated with a slight excess of bromine in petroleum ether solution (Pickles[8]) it yielded dibromo-myristicin-dibromide which crystallised from acetone-methyl-alcohol mixture as colourless prismatic needles and melted at 128–29° alone or in admixture with a sample made from natural myristicin.

Methylation : Elemicin (III)

The dihydroxy compound (6 g.) was methylated in anhydrous acetone solution (100 c.c.) with dimethyl sulphate (9 c.c.) and potassium carbonate (20 g.) by refluxing for six hours. The solvent was distilled off, the residue treated with water and the mixture extracted with ether. The ether extract was shaken with aqueous alkali, washed with water, dried over calcium

chloride and distilled. The residual liquid was distilled under reduced pressure (10 mm.) when elemicin passed over at 148–9°. It had a refractive index of 1·5245 at 31° for white light and 1·5240 at 30° and 1·5292 at 20° for the D line. Yield, 4 g. (Found: C, 69·3; H, 7·4; OCH_3, 45·1; $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7; OCH_3, 44·7%.)

The synthetic sample of elemicin was subjected to isomerisation with alcoholic potash and subsequent oxidation with alkaline permanganate (Semmler[9]). The product was found to be trimethyl gallic acid, identical with an authentic sample.

Summary

Employing the two stage process of ortho-oxidation eugenol is converted into 5-hydroxy eugenol. Methylation of this yields elemicin and methylenation myristicin. This constitutes the most convenient synthesis of these naturally occurring compounds and is highly significant from the point of view of biogenesis.

Note added in Proof.—After submitting the above paper for publication, the detailed paper of Trikojus and White on the "Synthesis of Myristicin" (*J.C.S.*, 1949, 436) was received. They have now recorded that even the isomeric pyrogallol-1-methyl-3-allyl ether (VIII) yields myristicin, apparently by migration of the allyl group to the meta-position.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXV. Isomers of Pedicinin

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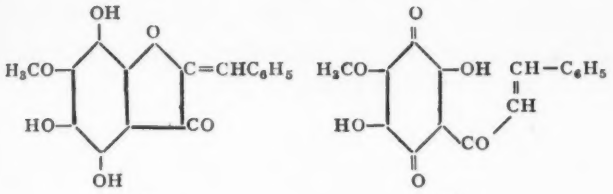
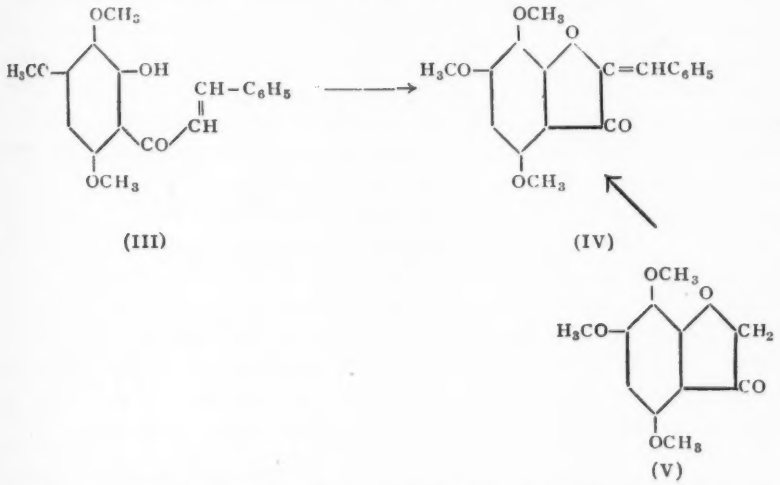
Pedicinin was first investigated by Sharma and Siddiqui[1] who proposed for it the constitution of 4: 5: 7-trihydroxy-6-methoxy-benzal-coumaran-3-one (I). This was based mainly on its molecular formula and its colour reaction with ferric chloride. Using this structure there was difficulty in explaining the conversion of pedicin and pedicellin into pedicinin. Later Bose and Dutt[2] found that pedicinin has quinone and acid properties and concluded that it should have the formula (II), *i.e.*, 2: 5-dihydroxy-4-methoxy-3: 6-quino-chalkone. In a subsequent publication Salooja, Sharma and Siddiqui[3] pointed out the existence of certain difficulties in the full acceptance of the new formula and contended that besides the quinone chalkone structure their original benzal-coumaranone formula was also necessary and that the substance should be considered to exhibit tautomerism. In the course of work in these laboratories on the formation of quinones by oxidative demethylation and on nuclear oxidation in flavones and related compounds fresh light was thrown on this question. Bose and Dutt's formula was definitely supported by the studies on oxidative demethylation[4] and most of the difficulties pointed out by Sharma and Siddiqui were eliminated by the establishment of the correct constitution of pedicin[5] and the isolation of the various stages in its transformation to pedicinin. Thus there seemed to be definite support for the quinone-chalkone formula and none for the benzal-coumaranone structure. But there was one point raised by Salooja, Sharma and Siddiqui[3] requiring further attention. It related to the existence of two melting points for pedicinin: (1) the sample obtained by the precipitation of pedicinin from its solution in aqueous alkali (potash) was found to melt at 207–208°, (2) but after crystallisation from an organic solvent (chloroform) the sample melted lower at 203–204°. These were considered to represent two tautomeric structures (I) and (II).

As a result of other work in progress in these laboratories it has now become possible to prepare synthetically 4: 5: 7-trihydroxy-6-methoxy-benzal-coumaranone (I) and compare it with pedicinin. The first stage i.



(I) (II)

the synthesis is the preparation of 4:6:7-trimethoxy-benzal-coumaranone (IV). The compound was easily obtained from 2-hydroxy-3:4:6-trimethoxy-chalkone[5] (III) by means of alkaline hydrogen peroxide. The nature of the reaction involved has been studied recently by Geissman, *et. al.*[7]; in the present case it gives a very good yield of the required benzal-coumaranone. The constitution of the product is confirmed by its preparation from 4:6:7-trimethoxy coumaranone (V) and benzaldehyde.

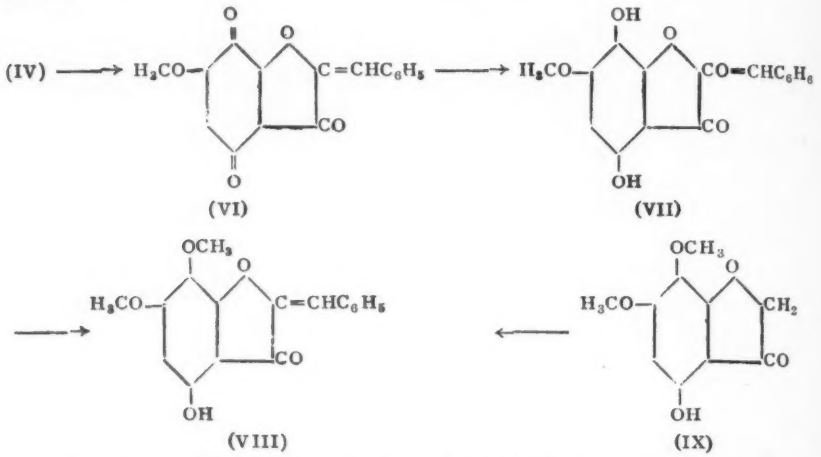


(III) (IV)

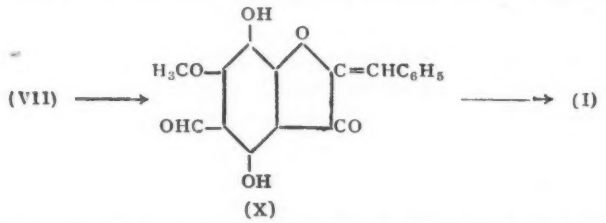
(V)

By treatment with cold nitric acid the above trimethoxy-benzal-coumaranone yields 6-methoxy-4:7-quino-benzal-coumaranone (VI) involving oxidative demethylation of the para-positions alone. In this respect the reaction resembles that of 5:7:8-methoxy-flavones[8]. Reduction with sulphur dioxide yields the corresponding quinol, 4:7-dihydroxy-6-methoxy-benzal coumaranone (VII). In support of the constitution of this compound it was partially methylated using the requisite quantity of dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium and the resulting 4-hydroxy-6:7-dimethoxy-benzal-coumaranone (VIII) was found to be

identical with the condensation product of benzaldehyde and 4-hydroxy-6:7-dimethoxy-coumaranone[6] (IX) obtained from gossypetol-tetramethyl-ether.



The next stage is ortho-oxidation of (VII) introducing a hydroxyl in the 5-position. This does not take place to any extent by means of alkaline persulphate but proceeds satisfactorily by the two stage process that has been recently studied in these laboratories. A further interesting point is that this quinol itself can directly be employed (see for the exploratory work Murti and Seshadri[9]). With hexamine in glacial acetic acid it gives a good yield of the 5-aldehyde (X) and subsequent oxidation with alkaline hydrogen peroxide produces the required 4:5:7-trihydroxy-6-methoxy-benzal-coumaranone (I). When the final product (I) is subjected to partial methylation using two moles of dimethyl sulphate a dimethyl ether (XII) is obtained which gives reactions for a free hydroxyl in the 4-position.

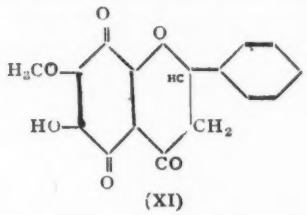


The properties of the pure product (I) are very different from those of either of the two samples obtained by Salooja, Sharma and Siddiqui. The most important differences are the low melting point, the lack of deep colour

and insolubility in sodium bicarbonate. Like all other benzal-coumaranones the new substance forms a deep blood-red colour with concentrated sulphuric acid. The differences are brought out in the following Table:—

	Pedicinin	4: 5: 7-Trihydroxy-6-methoxy-benzal-coumaranone
1. Solubility in alcohol ..	Fairly soluble	Sparingly soluble
2. Melting point ..	203–204° and 207–208°	182–83°
3. Crystal Structure ..	(i) Carmine-red stout rods and needles or (ii) Orange-red micro-crystalline powder	Bright yellow small prisms
4. Alcoholic erric fchloride ..	Deep reddish brown	Pale brown slowly changing to deep brown
5. Sodium carbonate or Ammonia ..	Orange-red to deep red solution	Yellow solution, sparingly soluble
6. Sodium bicarbonate ..	Orange solution	Insoluble

The explanation for the observation of Salooja, Sharma and Siddiqui regarding the two melting points for pedicinin should therefore be sought elsewhere. A plausible alternative would be the quino-flavanone isomer (XI) because of the known easy interconversion of chalkones and flavanones. A substance of this constitution (XI) was recently prepared by Rao, Rao and Seshadri[10] by the gentle oxidation of dihydro-pedicinin with *p*: benzoquinone and the name allo-pedicinin given to it. But its properties are also very different from either of the two forms of pedicinin described by Salooja, *et. al.* Its melting point was also too low (183–84°).



(XI)

We had occasion to repeat the experiments of Salooja, Sharma and Siddiqui regarding the melting points of pedicinin and we confirm their findings; but we also noticed that a mixture of the two samples melted in between and there was no depression thus showing that they were not really two different substances. It appeared to be possible that the formation of a small amount of allo-pedicinin by cyclisation during the heating involved in the crystallisation may account for the small lowering of the melting point of the cyrstallised sample. But no further lowering of the melting point could be brought about by longer heating of the chloroform solution. It

is rather remarkable that even when we heated an acidified alcoholic solution of pedicinin for two hours no change could be observed. Much longer heating of this solution (30 hours) produced some resinification, but pedicinin was recovered substantially unchanged. Hence this explanation involving flavanone conversion for the dual melting point is not satisfactory. A simple possibility is that pedicinin may be capable of existing in two crystal forms having two different melting points. The use of the term isopedicinin[3] in this connection does not seem to be therefore justified.

Experimental

2-Hydroxy-3 : 4 : 6-trimethoxy-chalkone[5] (III) was prepared from 2-hydroxy-3 : 4 : 6-trimethoxy-acetophenone and benzaldehyde.

4 : 6 : 7-*Trimethoxy-benzal-coumaran-3-one* (*IV*)

(1) The above chalkone (III) (2·0 g.) was dissolved in alcohol (100 c.c.) and sodium hydroxide (5%; 15 c.c.) added. To this solution hydrogen peroxide (6%; 10 c.c.) was added drop by drop with shaking. The mixture was allowed to stand for two hours and diluted with water and the solid that separated out was filtered and crystallised from alcohol. It was obtained as straw-yellow rectangular plates melting at 180–81°. Yield, 1·6 g. (Found: C, 68·8; H, 5·2; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%.)

With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous alkali. It gave a blood-red colour with concentrated sulphuric acid.

(2) To an ice-cooled dry ether solution of 1 : 2 : 3 : 5-tetramethoxy-benzene (10 c.c.) anhydrous aluminium chloride (20 g.) and chloracetyl chloride (7 c.c.) were added carefully (see Balakrishna, Rao and Seshadri[6]). The mixture was set aside overnight and then decomposed by carefully adding water (100 c.c.) and concentrated hydrochloric acid (50 c.c.) and heating the mixture on a boiling water-bath for half-an-hour. The semi-solid product was extracted with ether, the ether extract concentrated and the residue obtained was boiled with sodium acetate solution (10%). The trimethoxy-coumaranone (V) was extracted with ether and the ether extract distilled; a colourless liquid was obtained which did not solidify at room temperature. It (2 c.c.) was heated with benzaldehyde (3 c.c.) and concentrated sulphuric acid (a few drops) at 60°. The reaction mixture was diluted with water and allowed to stand overnight. The product that separated out was filtered and crystallised from alcohol. It was obtained as yellow rectangular plates melting at 180–81° and was identical with the product obtained by method (1); the mixed melting point was not depressed

6-Methoxy-4: 7-quino-benzal-coumaranone (*VI*)

The above trimethoxy compound (IV) (1·6 g.) was treated with nitric acid (15 c.c.; d., 1·2) in the cold (20–25°) for 15 minutes and the mixture diluted with water. The solid product that separated out was filtered. It crystallised from alcohol as yellow plates melting at 164–65°. Yield, 1·2 g. (Found: C, 68·2; H, 3·9; $C_{16}H_{10}O_5$ requires C, 68·1; H, 3·6%.) With alcoholic ferric chloride it did not give any colour but with concentrated sulphuric acid a bright red colour was produced.

6-Methoxy-4: 7-dihydroxy-benzal-coumaranone (*VII*)

Sulphur dioxide was passed through an alcoholic solution of the above quinone (VI) (1·0 g.) for about 15 minutes. On concentrating the solution, the quinol separated out. It crystallised from alcohol as yellow elongated rectangular plates melting at 185–86°. Yield, 0·8 g. (Found: C, 67·3; H, 3·9; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%.) It was soluble in aqueous alkali. With alcoholic ferric chloride it gave a brown colour and with concentrated sulphuric acid a blood-red colour.

6: 7-*Dimethoxy-4-hydroxy-benzal-coumaranone* (*VIII*)

(*a*) The above dihydroxy compound (VII) (0·2 g.) was boiled with dimethyl sulphate (0·1 c.c.) and anhydrous potassium carbonate (5·0 g.) in dry acetone medium (25 c.c.) for six hours. The resulting 4-hydroxy-compound (VIII) crystallised from alcohol as yellow prismatic rods melting at 177–78°. (Found: C, 68·2; H, 5·0; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%.)

(*b*) 4-Hydroxy-6: 7-dimethoxy-coumaranone[6] (IX) (0·5 g.), obtained from gossypetol-tetra-methyl-ether, was heated at 60° with benzaldehyde (0·8 c.c.) and a few drops of concentrated sulphuric acid for 2 hours. The mixture was diluted with water. After allowing it to stand overnight the product that separated out was filtered and crystallised from alcohol. It was identical with the sample obtained by the method given under (*a*); the mixed melting point was undepressed.

6-Methoxy-4: 7-dihydroxy-5-aldehydo-benzal-coumaranone (*X*)

The above quinol (VII) (1·5 g.) was dissolved in glacial acetic acid (10 c.c.) and hexamine (5·0 g.) added. The solution was kept gently boiling for 6 hours. Concentrated hydrochloric acid (20 c.c.) was added and the mixture heated to boiling and allowed to cool. The yellow solid that separated out was filtered. It crystallised from alcohol as lemon-yellow rectangular plates melting at 191–92°. Yield 1·0 g. (Found: C, 65·2; H, 4·0; $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·8%.)

With alcoholic ferric chloride it gave a brown colour and was soluble in aqueous alkali. With concentrated sulphuric acid a deep red colour was produced. It condensed with phenylhydrazine in alcohol containing a few drops of glacial acetic acid to form a yellow phenyl-hydrazone which crystallised from alcohol as rectangular plates melting at 145–46°. (Found: C, 69·1; H, 4·2; $C_{23}H_{18}O_5N_2$ requires C, 68·7; H, 4·5%.)

4: 5 : 7-*Trihydroxy*-6-*methoxy-benzal-coumaranone* (*I*)

The above aldehyde (X) (0·6 g.) was dissolved in alcohol (50 c.c.) and the solution was treated alternately with sodium hydroxide (5%; 15 c.c.) and hydrogen peroxide (6%; 10 c.c.) added in small quantities. After allowing it to stand for an hour the solution was diluted with water and the solid product that separated out filtered. It crystallised from alcohol as yellow short needles melting at 182–83°. Yield, 0·3 g. (Found: C, 63·8; H, 4·1; OCH_3, 10·0, $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0, OCH_3, 10·3%.) With alcoholic ferric chloride it gave a brown colour and was soluble in aqueous potash. It was very sparingly insoluble in aqueous sodium carbonate and insoluble in sodium bicarbonate solution. A blood-red colour was produced with concentrated sulphuric acid.

4-*Hydroxy*-5: 6: 7-*trimethoxy-benzal-coumaranone* (*XII*)

The above trihydroxy compound (I) (0·3 g.) was dissolved in dry acetone (25 c.c.) and treated with dimethyl sulphate (0·2 c.c.) and anhydrous potassium carbonate (5·0 g.). The mixture was refluxed for 6 hours and the potassium salts were filtered off. The filtrate was concentrated and the residue crystallised from alcohol. It was obtained as yellow rectangular plates melting at 152–53°. (Found: C, 66·0; H, 5·1; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). With alcoholic ferric chloride it gave a brown colour and was sparingly soluble in aqueous sodium hydroxide.

Summary

The structure of 6-methoxy-4: 5: 7-trihydroxy-benzal-coumaranone was suggested by Salooja *et. al.*[3] for one of the forms of pedicinin. A substance of this constitution has now been synthesised by applying the two stage process of nuclear oxidation to an appropriate compound of the benzal-coumaranone series. The synthetic product differs markedly from pedicinin. Similar difference has been noticed earlier with the flavanone isomer, allo-pedicinin. It is concluded therefore that the two melting points noted for pedicinin are due to the existence of two crystal forms.

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RAMAN AND INFRA-RED SPECTRA OF β-QUARTZ

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1. INTRODUCTION

RAMAN SPECTRUM of β-quartz has recently been obtained by Narayanaswamy (1948). He finds that the frequency 466 of α-quartz appears as 452·5, while the frequencies 207, 356 and 1082 of α-quartz are absent from the spectrum. In addition he finds frequencies at 97, 250, 395, 686, 792, 1060 and 1154 cm.$^{-1}$ which correspond to the frequencies 128, 265, 394–403, 695, 795–807, 1063 and 1159 in α-quartz. These facts have been explained on group theoretical considerations, and in addition we have predicted corresponding results for the infra-red spectrum. By taking only three force-constants, namely those of Si—O valence, $^{O}\!\diagdown$Si—O deformation and O—O repulsion all the frequencies of β-quartz have been calculated. These values agree approximately with the observed ones.

2. CHARACTER TABLE

β-Quartz is hexagonal, the symmetry class being hexagonal enantiomorphic hemihedral pertaining to the point-group D_6 of the Schonflies notation. The structure accordingly has in addition to a six-fold axis, six two-fold axes of symmetry. The repeating unit contains three silicon and six oxygen atoms whose positions with reference to hexagonal axes (a, a, c) are given by

Silicon (1, 2, 3) in order $(u, 0, 0)$, $(0, u, -\frac{1}{3})$, $(\bar{u}, \bar{u}, \frac{1}{3})$;

Oxygen (4, 5, 6, 7, 8, 9) in order (x, y, z), $(y, x, \bar{z} + \frac{2}{3})$, $(\bar{y}, x - y, z - \frac{1}{3})$, $(\bar{x}, y - x, \bar{z} + \frac{1}{3})$, $(y - x, \bar{x}, z - \frac{2}{3})$, $(x - y, \bar{y}, \bar{z})$.

The structure of β-quartz was established by W. H. Bragg and R. E. Gibbs (1925) and by Wyckoff (1926). We have adopted the structure given by the former. They have not given any co-ordinates but according to them the value of q, *i.e.*, the distance of the oxygen atom from the middle point of the line joining the silicon atoms is ·35 A.U. Using $a = 5{\cdot}01$ A.U. and $c = 5{\cdot}466$ A.U. (Jay, 1933; and Landolt Tables) we get the following co-ordinates for atoms in rectangular axis which are given in Table I.

TABLE I

		x	y	z
1	Si ..	2·505	0	0
4	O ..	1·5754	·9097	− ·911
3′	Si ..	1·2525	2·1693	−1·822
5	O ..	0	1·8193	−2·733
2	Si ..	−1·2525	2·1693	1·822
6	O ..	−1·5754	·9097	·911
1′	Si ..	−2·505	0	0
7	O ..	−1·5754	− ·9097	− ·911
3	Si ..	−1·2525	−2·1693	−1·822
8	O ..	0	−1·8193	−2·733
2′	Si ..	1·2525	−2·1693	1·822
9	O ..	1·5754	− ·9097	·911

These correspond to $u = \cdot 5\,a$, $x = \cdot 2094\,a$, $y = -\cdot 2101\,a$, and $z = c/6$ in hexagonal axes and they agree with those given in Landolt Tables, namely $u = \cdot 5\,a$, $x = \cdot 21\,a$, $y = -\cdot 21\,a$, and $z = c/6$.

In order to bring out the full hexagonal symmetry we take the unit cell (Fig. 1) containing six silicon atoms 1, 2, 3 and 1′, 2′, 3′, and six oxygen

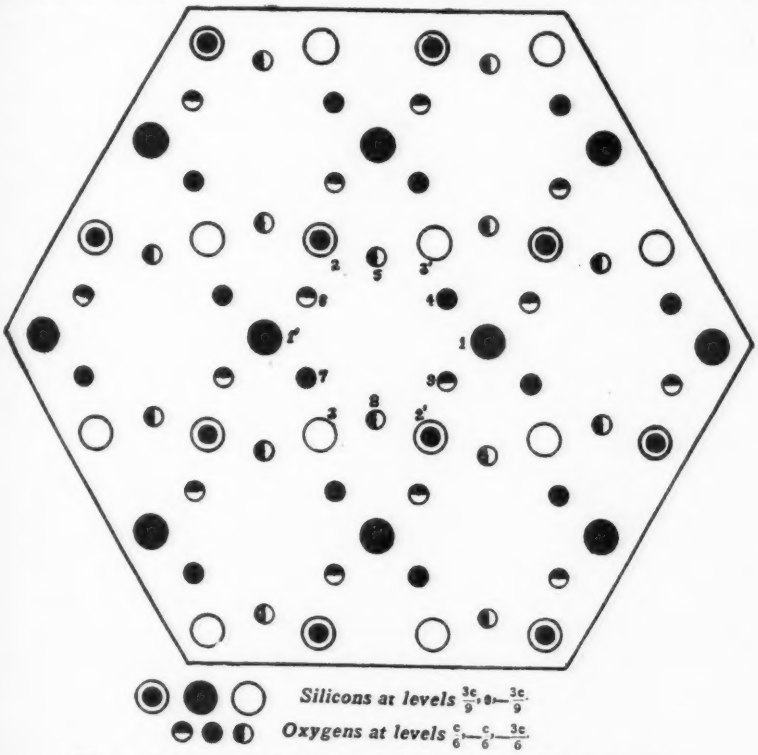

FIG. 1. Projection of the Structure of β-quartz on the basal plane

atoms 4, 5, 6, 7, 8 and 9. Each silicon atom is shared between two cells. For the complete analysis of the vibrations of this system, which give rise to the Raman spectrum of the first order and the infra-red spectrum, we proceed on the assumption that the vibrations of atoms within a cell of a crystal lattice have exactly the same frequency and phase as the vibrations in the neighbouring cells. This is immediately satisfied if we use the condition that the equivalent points of the lattice have the same displacements at any given instant. Thus the displacements of silicon atoms 1′, 2′, 3′ should always be the same as those of the silicon atoms 1, 2, 3, respectively. Therefore those vibrations will not be permitted in which these atoms are moving in opposite phases.

Considering now the group of six silicon and six oxygen atoms in the unit cell, we should have 36 vibrations in all ; but due to the restriction mentioned above, only 27 will be permitted, which correspond to the modes of vibrations of the group $3SiO_2$. The nine not-permitted modes can be easily found out by writing the symmetry modes and picking out those in which the movement of silicon atoms 1, 2, 3 are opposite in phase to those of 1′, 2′, 3′ respectively. Of these nine not-permitted modes three, namely Q_1', Q_5', Q_{12}' are non-degenerate and three namely Q_{17}', Q_{19}', Q_{20}' are doubly degenerate.

The total number of vibrations are divided into six classes: one totally symmetric, three antisymmetric and two degenerate. The number of vibrations in each class and their selection rule in the Raman and Infra-red spectra are easily calculated by Group Theory method and are given below in Table II.

TABLE II

D_6	E	$2C_6^z$	$2C_3^z$	C_2^z	$3C_2^x$	$3C_2^y$	No. of vibrations	No. not permitted	No. allowed	Translations	Allowed internal modes	Selection Rules	
												Raman	Infra-red
A ..	1	1	1	1	1	1	2	1	1	..	1	p	f
B ..	1	1	1	1	−1	−1	4	1	3	$1_{(Q_z)}$	2	f	$p_{(M_z)}$
C ..	1	−1	1	−1	1	−1	3	0	3	..	3	f	f
D ..	1	−1	1	−1	−1	1	3	1	2	..	2	f	f
E_1 ..	2	1	−1	−2	0	0	6	1	5	$1_{(Q_x, Q_y)}$	4	p	$p_{(M_x, M_y)}$
E_2 ..	2	−1	−1	2	0	0	6	2	4	..	4	p	f
n_R ..	12	0	0	0	2	2							
ϵ_R ..	36	0	0	0	−6	−6							

Table II shows that nine vibrations are permitted in the Raman effect and six in the infra-red. Of these only four appear both in the Raman effect

and in the infra-red. Comparing the corresponding data for α-quartz (Saksena, 1940) we find that twelve vibrations appear in the Raman effect and twelve in the infra-red and of these only eight appear both in the Raman effect and in the infra-red.

3. Symmetry Modes

The symmetry modes of these vibrations are given below. It may be seen that the symmetry modes are almost the same as those for α-quartz if the angle ' α ' used in the latter case is taken as 90°.

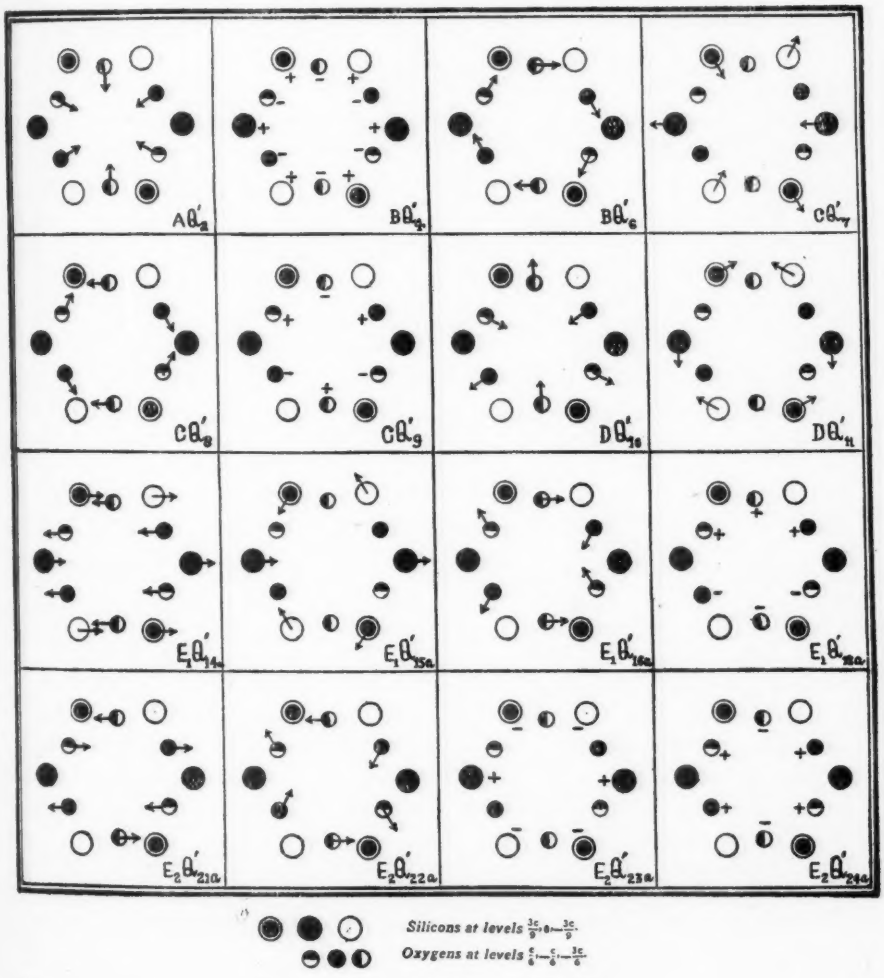

Fig. 2. Symmetry modes of β-quartz

The method of writing the symmetry modes is the same as used in α-quartz. They are stated in terms of the co-ordinates x_i, y_i, z_i, which are the co-ordinates of the ith atom with the equilibrium position as the origin. Each x_i points towards a point in the basal plane where the six-fold axis meets it, z_i is perpendicular to the plane, and y_i at right angles to both and is positive in a direction so as to make the motion right-handed. The symmetry modes are graphically shown in Fig. 2.

Class Modes

A^2

$Q_1' \rightarrow x_1+x_2+x_3+x_1'+x_2'+x_3'$ not permitted

$Q_2' \rightarrow x_4+x_5+x_6+x_7+x_8+x_9$

B^4

$Qz \rightarrow m_{Si}^{\frac{1}{2}}(z_1+z_2+z_3+z_1'+z_2'+z_3')+m_0^{\frac{1}{2}}(z_4+z_5+z_6+z_7+z_8+z_9)$

$Q_4' \rightarrow m_0^{\frac{1}{2}}(z_1+z_2+z_3+z_1'+z_2'+z_3') - m_{Si}^{\frac{1}{2}}(z_4+z_5+z_6+z_7+z_8+z_9)$

$Q_5' \rightarrow y_1+y_2+y_3+y_1'+y_2'+y_3'$ not permitted

$Q_6' \rightarrow y_4+y_5+y_6+y_7+y_8+y_9$

C^3

$Q_7' \rightarrow x_1+x_2+x_3-x_1'-x_2'-x_3'$

$Q_8' \rightarrow y_4+y_6+y_8-y_5-y_7-y_9$

$Q_9' \rightarrow z_4+z_6+z_8-z_5-z_7-z_9$

D^3

$Q_{10}' \rightarrow x_4+x_6+x_8-x_5-x_7-x_9$

$Q_{11}' \rightarrow y_1+y_2+y_3-y_1'-y_2'-y_3'$

$Q_{12}' \rightarrow z_1+z_2+z_3-z_1'-z_2'-z_3'$ not permitted

E_1^6

$$Q_x \rightarrow m_{Si}^{\frac{1}{2}}[(-2x_1+x_2+x_3+2x_1'-x_2'-x_3') + \sqrt{3}(y_2-y_3-y_2'+y_3')] + m_0^{\frac{1}{2}}[\sqrt{3}(-x_4+x_6+x_7-x_9)+(y_4+2y_5+y_6-y_7-2y_8-y_9)]$$

$$Q_y \rightarrow m_{Si}^{\frac{1}{2}}[\sqrt{3}(-x_2+x_3+x_2'-x_3')-(2y_1-y_2-y_3-2y_1'+y_2'+y_3')] + m_0^{\frac{1}{2}}[(-x_4-2x_5-x_6+x_7+2x_8+x_9)+\sqrt{3}(-y_4+y_6+y_7-y_9)]$$

$$Q_{14a}' \rightarrow m_0^{\frac{1}{2}}[(-2x_1+x_2+x_3+2x_1'-x_2'-x_3') + \sqrt{3}(y_2-y_3-y_2'+y_3')] - m_{Si}^{\frac{1}{2}}[\sqrt{3}(-x_4+x_6+x_7-x_9)+(y_4+2y_5+y_6-y_7-2y_8-y_9)]$$

$$Q_{14b}' \rightarrow m_0^{\frac{1}{2}}[\sqrt{3}(-x_2+x_3+x_2'-x_3')-(2y_1-y_2-y_3-2y_1'+y_2'+y_3')] - m_{Si}^{\frac{1}{2}}[(-x_4-2x_5-x_6+x_7+2x_8+x_9)+\sqrt{3}(-y_4+y_6+y_7-y_9)]$$

$$Q_{15a}' \rightarrow (-2x_1+x_2+x_3+2x_1'-x_2'-x_3') - \sqrt{3}(y_2-y_3-y_2'+y_3')$$

Class — Modes

$Q_{15b}' \rightarrow (2y_1-y_2-y_3-2y_1'+y_2'+y_3') - \sqrt{3}\,(x_2-x_3-x_2'+x_3')$

$Q_{16a}' \rightarrow (y_4+2y_5+y_6-y_7-2y_8-y_9) - \sqrt{3}\,(-x_4+x_6+x_7-x_9)$

$Q_{16b}' \rightarrow (-x_4-2x_5-x_6+x_7+2x_8+x_9) - \sqrt{3}\,(-y_4+y_6+y_7-y_9)$

$Q_{17a}' \rightarrow (z_2-z_3-z_2'+z_3')$ } not permitted

$Q_{17b}' \rightarrow (2z_1-z_2-z_3-2z_1'+z_2'+z_3')$ } not permitted

$Q_{18a}' \rightarrow (z_4+2z_5+z_6-z_7-2z_8-z_9)$

$Q_{18b}' \rightarrow (z_4-z_6-z_7+z_9)$

E_2^6

$Q_{19a}' \rightarrow (-2x_1+x_2+x_3-2x_1'+x_2'+x_3')+\sqrt{3}\,(y_2-y_3+y_2'-y_3')$ } not permitted

$Q_{19b}' \rightarrow (2y_1-y_2-y_3+2y_1'-y_2'-y_3')-\sqrt{3}\,(-x_2+x_3-x_2'+x_3')$ } not permitted

$Q_{20a}' \rightarrow (2y_1-y_2-y_3+2y_1'-y_2'-y_3') - \sqrt{3}\,(x_2-x_3+x_2'-x_3')$ } not permitted

$Q_{20b}' \rightarrow (-2x_1+x_2+x_3-2x_1'+x_2'+x_3')-\sqrt{3}\,(y_2-y_3+y_2'-y_3')$ } not permitted

$Q_{21a}' \rightarrow (y_4-2y_5+y_6+y_7-2y_8+y_9) + \sqrt{3}\,(-x_4+x_6-x_7+x_9)$

$Q_{21b}' \rightarrow (-x_4+2x_5-x_6-x_7+2x_8-x_9) + \sqrt{3}\,(-y_4+y_6-y_7+y_9)$

$Q_{22a}' \rightarrow (y_4-2y_5+y_6+y_7-2y_8+y_9) - \sqrt{3}\,(-x_4+x_6-x_7+x_9)$

$Q_{22b}' \rightarrow (-x_4+2x_5-x_6-x_7+2x_8-x_9) - \sqrt{3}\,(-y_4+y_6-y_7+y_9)$

$Q_{23a}' \rightarrow 2z_1-z_2-z_3+2z_1'-z_2'-z_3'$

$Q_{23b}' \rightarrow z_2-z_3+z_2'-z_3'$

$Q_{24a}' \rightarrow z_4-2z_5+z_6+z_7-2z_8+z_9$

$Q_{24b}' \rightarrow z_4-z_6+z_7-z_9$

4. Comparison of Symmetry Modes in α-Quartz and β-Quartz

There are only three classes in α-quartz—one totally symmetric containing four modes, one non-degenerate containing four modes and one doubly degenerate containing eight modes. As the vibrating unit in α- and β-quartz is the same (3 SiO_2), the vibrations in β-quartz will be of the same type as in α-quartz but will divide into different classes due to increased symmetry. Taking the totally symmetric class of α-quartz it can be immediately seen that only the mode Q_2' can persist in totally symmetric class A of β-quartz due to the presence of the six-fold axis, and the remaining three Q_1', Q_3', Q_4' must go to class C in β-quartz due to anti-symmetry with respect to the six-fold axis and symmetry with respect to three two-fold electric

axes (x axes). Similarly the four modes Q_6', Q_7', Q_8', Q_9' in the anti-symmetric class in α-quartz will split up into two classes B and D due to the presence of the six-fold axis of symmetry. Two of these vibrations which are symmetric to the six-fold axis, namely Q_7', Q_9' will remain in class B of β-quartz. The remaining two Q_6', Q_8' will go to class D due to being anti-symmetric to the six-fold axis and also to the three two-fold electric axes (*i.e.*, x axes), and symmetric with respect to three two-fold mechanical axes (*i.e.*, y axes) On this basis the number of normal modes in the classes A, B, C and D of β-quartz becomes 1, 2, 3 and 2 respectively as is also shown in the character table.

Coming to the eight degenerate modes in α-quartz we see that they divide into two classes E_1, E_2 in β-quartz due to anti-symmetry and symmetry with respect to the two-fold z axis of symmetry. It can be seen by studying the modes that four come in each class. The comparison of these modes in β-quartz with those in α-quartz is given in Table III, which also contains the frequencies assigned by one of us to the various modes in α-quartz. This gives us an idea of the frequencies that are to be expected in various classes in β-quartz.

TABLE III

Class	Symmetry mode in β-quartz	Corresponding symmetry mode in α-quartz	Frequency assigned in α-quartz	Frequency observed in β-quartz
A ..	Q_2'	Q_2'	466	452·5
B ..	Q_4'	Q_7'	508	
	Q_6'	Q_9'	1149	
C ..	Q_7'	Q_1'	207	
	Q_8'	Q_3'	1082	
	Q_9'	Q_4'	356	
D ..	Q_{10}'	Q_6'	777	
	Q_{11}'	Q_8'	364	
E_1 ..	Q_{14}'	Q_{11}'	479	
	Q_{15}'	Q_{12}'	128	97
	Q_{16}'	Q_{15}'	1159	1154
	Q_{18}'	Q_{16}'	265	250
E_2 ..	Q_{21}'	Q_{13}'	695	686
	Q_{22}'	Q_{14}'	392—403	395
	Q_{23}'	Q_{18}'	1063	1060
	Q_{24}'	Q_{17}'	807	792

5. Calculation of Frequencies

By using four force-constants, namely those of Si—O valence (K), of $^{Si}\!\diagdown$O—Si and $^{O}\!\diagdown$Si—O deformations (K_1, and K_2 respectively) and of O—O repulsion (K_3) the potential energy may be written as

$$2V = K\Sigma_{12}(\Delta r)^2 + K_1\Sigma_6(\Delta\phi)^2 + \tfrac{1}{2}K_2\Sigma_{36}(\Delta\psi)^2 + \tfrac{1}{2}K_3\Sigma_{36}(\Delta R)^2,$$

where Δr and ΔR are the changes in the Si—O and O—O distances respectively, while $\Delta\phi$ and $\Delta\psi$ are the changes in the $^{Si}\!\diagdown$O—Si and O—Si—O angles respectively. At each silicon atom there are six O—O distances and six $^{O}\!\diagdown$Si—O angles and therefore, for finding out the potential energy of the unit cell which contains six silicon atoms we should consider thirty-six O—O distances and 36 $^{O}\!\diagdown$Si—O angles. But as each silicon is shared between two cells the contribution of each of these to the potential energy is to be halved. For the same reason the contribution of the silicon atoms to the kinetic energy is also to be halved.

The frequencies for the various classes are given below:—

Class A

$$\lambda^2 = \cdot00607\,K + \cdot09475\,K_1 + \cdot1421\,K_2 + \cdot1453\,K_3.$$

Class B

$$\lambda^4 - (\cdot1563\,K + \cdot1574\,K_2 + \cdot2318\,K_3)\,\lambda^2 + (\cdot02196\,KK_2 + \cdot01820\,KK_3 + \cdot02945\,K_2K_3) = 0$$

Class C

$$\begin{vmatrix} \cdot6852\,K + 1\cdot043\,K_2 - 14\cdot15\,\lambda^2 & \cdot9232\,K + \cdot061\,K_2 & \cdot6714\,K - \cdot5327\,K_2 \\ \cdot9232\,K + \cdot061\,K_2 & 1\cdot244\,K + \cdot00357\,K_2 + 1\cdot498\,K_3 - 16\,\lambda^2 & \cdot9046\,K - \cdot0312\,K_2 + 1\cdot732\,K_3 \\ \cdot6714\,K - \cdot5327\,K_2 & \cdot9046\,K - \cdot0312\,K_2 + 1\cdot732\,K_3 & \cdot658\,K + \cdot2719\,K_2 + 2\cdot003\,K_3 - 16\,\lambda^2 \end{vmatrix} = 0$$

On expansion it becomes

$$\lambda^6 - (\cdot1672\,K + \cdot0909\,K_2 + \cdot2188\,K_3)\,\lambda^4 + (\cdot0138\,KK_2 + \cdot01192\,KK_3 + \cdot01817\,K_2K_3)\,\lambda^2 = 0.$$

Class D

$$\begin{vmatrix} \cdot09714\,K + 1\cdot513\,K_1 + \cdot926\,K_2 + 1\cdot532\,K_3 - 16\,\lambda^2 & \cdot2524\,K - \cdot997\,K_1 - \cdot991\,K_2 \\ \cdot2524\,K - \cdot997\,K_1 - \cdot991\,K_2 & \cdot6561\,K + \cdot657\,K_1 + 1\cdot06\,K_2 - 14\cdot15\,\lambda^2 \end{vmatrix} = 0$$

Class E_1

$$\begin{vmatrix} 2\cdot908\,K + 3\cdot293\,K_1 + 4\cdot562\,K_2 - 36\cdot3\,\lambda^2 & \cdot0304\,K + \cdot5431\,K_1 + \cdot017\,K_2 & -1\cdot194\,K + 1\cdot581\,K_1 + \cdot9512\,K_2 & -1\cdot884\,K + 1\cdot493\,K_2 \\ \cdot0304\,K + \cdot5431\,K_1 + \cdot017\,K_2 & \cdot6707\,K + \cdot0896\,K_1 + 1\cdot053\,K_2 - 14\cdot15\,\lambda_2 & \cdot3353\,K + \cdot2608\,K_1 + \cdot5265\,K_2 & \cdot2332\,K - \cdot1851\,K_2 \\ -1\cdot194\,K + 1\cdot581\,K_1 + \cdot9512\,K_2 & \cdot3353\,K + \cdot2608\,K_1 + \cdot5265K_2 & \cdot6707\,K + \cdot759\,K_1 + \cdot4647\,K_2 + 1\cdot514\,K_3 - 16\,\lambda^2 & \cdot9049\,K + \cdot2208\,K_2 + 2\cdot368\,K_3 \\ -1\cdot884\,K + 1\cdot493\,K_2 & \cdot2332\,K - \cdot1851\,K_2 & \cdot9049\,K + \cdot2208\,K_2 + 2\cdot368\,K_3 & 1\cdot316\,K + \cdot5202\,K_2 + 3\cdot945\,K_3 - 32\,\lambda^2 \end{vmatrix} = 0$$

Class E_2

$$\begin{vmatrix} \cdot6706\,K + \cdot7584\,K_1 + \cdot9273\,K_2 + 2\cdot998\,K_3 - 16\,\lambda^2 & \cdot5735\,K - \cdot7584\,K_1 + \cdot0959\,K_2 + 2\cdot208\,K_3 & -\cdot6713\,K + \cdot1742\,K_1 + \cdot533\,K_2 & \cdot9046\,K - \cdot9346\,K_2 + 1\cdot731\,K_3 \\ \cdot5735\,K - \cdot7584\,K_1 + \cdot0959\,K_2 + 2\cdot208\,K_3 & \cdot6706\,K + \cdot7584\,K_1 + \cdot4582\,K_2 + 3\cdot014\,K_3 - 16\,\lambda^2 & -\cdot2333\,K - \cdot1742\,K_1 + \cdot1858\,K_2 & \cdot9046\,K - 1\cdot029\,K_2 + 2\cdot367\,K_3 \\ -\cdot6713\,K + \cdot1742\,K_1 + \cdot533\,K_2 & -\cdot2333\,K - \cdot1742\,K_1 + \cdot1858\,K_2 & 1\cdot316\,K + \cdot04\,K_1 + 2\cdot127\,K_2 - 28\cdot3\,\lambda^2 & -\cdot6582\,K - 1\cdot064\,K_2 \\ \cdot9046\,K - \cdot9346\,K_2 + 1\cdot731\,K_3 & \cdot9046\,K - 1\cdot029\,K_2 + 2\cdot367\,K_3 & -\cdot6582\,K - 1\cdot064\,K_2 & 1\cdot316\,K + 2\cdot92\,K_2 + 5\cdot948\,K_3 - 32\,\lambda^2 \end{vmatrix} = 0$$

As the Raman frequencies in β-quartz do not differ much from the Raman frequencies of α-quartz, the force constants in the two cases cannot be very different. We have therefore adopted nearly the same force constants for β-quartz as found for α-quartz. The force constants for α-quartz are $K = 4{\cdot}98 \times 10^5$, $K_1 = {\cdot}454 \times 10^{-11}$, $K_2 = 1{\cdot}565 \times 10^{-11}$ and $K_3 = {\cdot}892 \times 10^5$, while for β-quartz we use $K = 5{\cdot}0 \times 10^5$, $K_1 = 0$, $K_2 = 2{\cdot}0 \times 10^{-11}$, and $K_3 = -1{\cdot}0 \times 10^5$ dynes.

The observed and calculated frequencies are given in Table IV.

TABLE IV

Class	Calculated Frequencies	Observed Raman Frequencies in β-quartz	Raman and Infra-red frequencies of α-quartz*
A ..	537	453	
B ..	1149, 392	..	(1149), (508)
C ..	1125, 311, 0	Forbidden in Raman & infra-red	(1082), (356), (207)
D ..	814, 273	Forbidden in Raman & infra-red	(777), (364)
E_1 ..	1156, 891, 353, 50	1154, 792, 395, 97	
E_2 ..	952, 499, 367, 275	1060, 686, (479), 250	

* The frequencies in this column have been given for comparison with calculated values of classes B, C and D.

6. DISCUSSION

The frequencies in brackets are those observed in α-quartz at room temperatures. It may be seen from this table that the calculated frequencies are of the right order and agree approximately with those observed or expected. In classes A to D the frequencies are nearly the same as those to be expected on the basis of the assignment in Table III, with the exception of frequency 207 which reduces to zero with these force constants. We shall discuss this point at a later stage. For classes E_1 and E_2 the assignments are the same as those given in Table III with the exception of the low frequencies 250 and (479) which should come to Class E_2 in place of 395 and 686 which should go to class E_1. As there are eight modes in α-quartz in the degenerate class, the assignment of these frequencies to particular symmetry modes may not be quite accurate and the above change is possible. We thus see that the calculated values are in fair agreement with those to be expected. By taking the proper values of these force constants it is possible to get better agreement between the observed and calculated values, but as the infra-red data are not known, it has not been attempted.

These results show that of the four infra-red frequencies observed in α-quartz in the extraordinary ray, two namely 777 and 364 will be forbidden in β-quartz, and only two corresponding to 1149 and 508 will appear in the

infra-red. Also four Raman frequencies 1154, 792, 395 and 97 will appear in the infra-red in the ordinary ray while the remaining four, namely 1060, 686, 479 and 250 will not appear in the infra-red.

As regards the Raman spectrum we find from Table III that the four frequencies belonging to the totally symmetric class in α-quartz, namely 207, 356, 466 and 1082, only the frequency corresponding to 466 can persist in the totally symmetric class in β-quartz, while the other three which go to class C will be forbidden both in the Raman effect and the infra-red. This explains the observations of Narayanaswamy that the frequencies corresponding to 207, 356 and 1082 do not appear in the Raman effect of β-quartz. We also observe from Tables II and III that all the frequencies belonging to the degenerate class in α-quartz appear in the two degenerate classes of β-quartz. This also has been observed in the Raman effect of β-quartz.

Further, we notice from our calculations that with any values of the four force constants used, the frequency 207 reduces to zero in β-quartz. It may be that the force constants used are not enough to account for the frequencies, but as all the important force constants have been taken into consideration, there appears no doubt that this frequency diminishes considerably in β-quartz. It has been noticed by Narayanaswamy that there is a considerable diminution in this frequency with temperature even in α-quartz.

7. Summary

The methods of group theory have been applied for the analysis of the Raman and infra-red spectra of β-quartz. The frequencies fall into six classes A, B, C, D, E_1, and E_2, the number of frequencies in the various classes being 1, 2, 3, 2, 4, and 4 respectively. Classes E_1 and E_2 are doubly degenerate. Of the four frequencies belonging to the totally symmetric class in α-quartz, namely 207, 356, 466, and 1082, only the frequency corresponding to 466 (452·8) can persist in the totally symmetric class in β-quartz and the remaining three should be forbidden in the Raman and infra-red spectrum. Further all the frequencies belonging to the degenerate class in α-quartz appear in the two degenerate classes in β-quartz. Both these facts have been observed in the Raman spectrum of β-quartz.

As regards the infra-red spectrum the results show that the four frequencies observed in α-quartz in the extraordinary ray, two only, namely 777 and 364 will be forbidden in β-quartz. Also of the eight degenerate frequencies only four will appear in the infra-red in the ordinary ray and the remaining four will not be active in the infra-red. The frequencies appearing in the infra-red according to our calculations are 1154, 792, 395 and 97

and those forbidden are 1060, 686, 479 and 250. The infra-red spectrum has not been observed.

We have also developed the formulæ for calculating the frequencies with the help of four force constants, namely K of Si—O valence, K_1 and K_2 of $^{Si}\backslash O—Si$ and $^{O}\backslash Si—O$ deformation and K_3 of O—O repulsion. As the Raman frequencies in β-quartz do not differ much from the Raman frequencies of α-quartz we have adopted nearly the same force constants, namely $K = 5{\cdot}0 \times 10^5$, $K_1 = 0$, $K_2 = 2{\cdot}0 \times 10^{-11}$, $K_3 = -1 \times 10^5$ dynes. The frequencies calculated are

Class A 537 [453]; Class B 1149, 392 (1149, 508);

Class C 1125, 311, 0 (1082, 356, 207); Class D 814, 273 (777, 364);

Class E_1 1156, 891, 353, 50 [1154, 792, 395, 97]; and

Class E_2 952, 499, 367, 275 [1060, 686, (479), 250].

The frequencies in the brackets [ ] are the observed Raman frequencies of β-quartz while the frequencies in the brackets ( ) are the infra-red and Raman frequencies of α-quartz, given for comparison.

The frequency 207 diminishes very considerably in β-quartz. This is in agreement with the observed fact that this frequency diminishes considerably with temperature even in α-quartz.

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THE REFRACTIVE DISPERSIVE POWER OF ORGANIC COMPOUNDS

Part II. The Camphor-β-sulphonates (*d*- and *dl*-) of *o*-, *m*-, *p*-Toluidines, *o*-, *m*-, *p*-Iodanilines, α-Amino-pyridine, α- Aminothiazole, *p*-Aminobenzenesulphonamide and 6-Methoxy-8-aminoqinoline

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In Part I of this series of investigations,[1] the refractive dispersion of dextro, lævo and racemic forms of several terpene derivatives was described. It was pointed out that the earlier formulæ of Gladstone and Dale[2] $\left(\frac{n-1}{d}\right)$ and of Lorenz and Lorentz,[3] $\frac{n^2-1}{(n^2+1)d}$ for refractive power were defective as they do not take into account the effects of dispersion. This difficulty was removed by the work of Maxwell and Sellmeier[4] who proposed the dispersion formula as

$$n^2 = a^2 + \Sigma \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}. \qquad \text{(i)}$$

It is found that generally one term of the summation in this equation when added to a constant a^2 is sufficient to represent correctly the refractive dispersive power of different types of organic compounds of varying complexity.

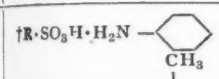
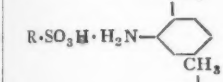
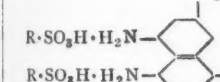
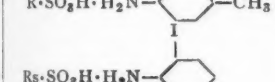
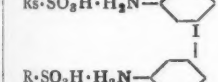
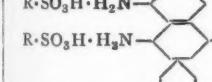
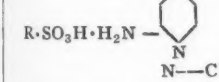
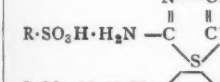
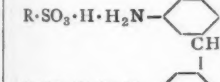
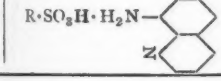
In this paper we record the results of our experiments on the refractive dispersion of the camphor-β-sulphonates (*d*- and *dl*-) of eleven aromatic and heterocyclic primary amines in aqueous solution (Tables II–XII). The refractive dispersion of these salts can be satisfactorily expressed by the Maxwell-Sellmeier simplified expression,

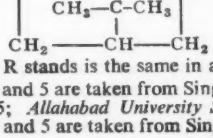
$$n^2 = a^2 + \frac{b_0\lambda^2}{\lambda^2 - \lambda_0^2}, \qquad \text{(ii)}$$

in which b_0 is the refraction constant and λ_0^2 the dispersion constant. The constant term a^2, when added to one term of the summation in equation (i), namely, $\frac{b_0\lambda^2}{\lambda^2 - \lambda_0^2}$ gives the square of the refractive index of the medium for a stationary electric field. The values of $\lambda_0 s$—the wavelengths of the

TABLE I

Comparative Tabular Statement of Values of (1) "*Absolute*" *Rotation* (*Drude Equation*); (2) "*Absolute*" *Refractive Index* (*Maxwell-Sellmeier Equation*); (3) *the Wavelength of the* "*Characteristic*" *Absorption Band* (λ_0) *from Drude and Maxwell-Sellmeier Equations in A°.U.*

1	2	3	4	5	6	7	8
No.	Compound	$[\alpha]^{38°}_{abs} = k_0$ (Drude Equation for $\lambda = \sqrt{1+\lambda_0^2}$)	$n^{38°}_{abs} = \sqrt{a^2 + b_0(1+\lambda_0^2)}$ (Maxwell-Sellmeier Equation for $\lambda = \sqrt{1+\lambda_0^2}$)	λ_0 (From Drude Equation)	λ_0 (from Maxwell-Sellmeier Equation)	λ_0 (Mean value of columns 5 and 6)	Difference of columns 5 and 6
1[a]	†R·SO_3H·H_2N— 	3·400	1·3301	3606	3620	3613	−14
2[a]	R·SO_3H·H_2N— 	3·367	1·3284	3562	3540	3551	+22
3[a]	R·SO_3H·H_2N— 	3·310	1·3285	3536	3533	3534	+3
4[a]	R·SO_3H·H_2N— 	3·390	1·3289	3597	3571	3584	+26
5[b]	Rs·SO_3H·H_2N— 	3·110	1·3316	3669	3659	3664	+10
6[b]	R·SO_3H·H_2N— 	3·268	1·3319	3664	3667	3666	−3
7[b]	R·SO_3H·H_2N— 	3·207	1·3319	3658	3637	3647	+21
8[c]	R·SO_3H·H_2N— 	3·367	1·3292	3289	3292	3290	−3
9[c]	R·SO_3H·H_2N— 	4·155	1·3297	3537	3544	3540	−7
10[d]	R·SO_3·H·H_2N— 	2·793	1·3301	3668	3676	3672	−8
11[c]	R·SO_3H·H_2N—	3·294	1·3290	3131	3172	3151	−41

† R = $C_{10}H_{15}O$ or 

The abbreviation for which R stands is the same in all the Tables I to XII.

[a] The values in columns 3 and 5 are taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, **6**, 15; *Allahabad University Studies*, 1944, 37.

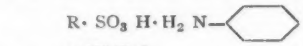
[b] The values in columns 3 and 5 are taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, **29**, 107.

[c] The values in columns 3 and 5 are taken from Singh, B. K., and Manhas, K. M. S., *Ibid.*, 1947, **26**, 61.

[d] The values in columns 3 and 5 are taken from Singh, B. K., and Perti, O. N., *Ibid.*, 1945, **22**, 84.

TABLE II

Refractive Dispersion of Anilinocamphor-β-sulphonates



$$\left\{ n^2 = 1{\cdot}7578 + \frac{0{\cdot}01121\lambda^2}{\lambda^2 - 0{\cdot}1311}; \quad \lambda_0^2 = 0{\cdot}1311,\ \lambda_0 = 0{\cdot}3606 \right\}$$

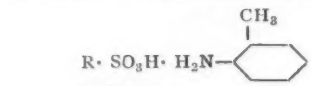
$$\left\{ [\alpha]^* = \frac{3{\cdot}400}{\lambda^2 - 0{\cdot}1300}; \quad \lambda_0^2 = 0{\cdot}1300,\ \lambda_0 = 0{\cdot}3620 \right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3314	1·3317	+0·0003	1·3316	+0·0002	+0·0001
Na_{5893} ..	1·3322	1·3324	+0·0002	1·3321	−0·0001	+0·0003
Hg_{5780} ..	1·3324	1·3324	±0·0000	1·3324	±0·0000	±0·0000
Hg_{5461} ..	1·3330	1·3331	+0·0001	1·3330	±0·0000	+0·0001
Hg_{4358} ..	1·3390	1·3389	−0·0001	1·3390	±0·0000	−0·0001

* The rotatory dispersion equation is taken from Singh, Perti and Singh, *Proc. Lahore Phil. Soc.*, 1944, **6**, 15 ; *Allahabad University Studies*, 1944, **37**, 57.

TABLE III

Refractive Dispersion of o-Toluidinocamphor-β-sulphonates



$$\left\{ n^2 = 1{\cdot}7506 + \frac{0{\cdot}01326\lambda^2}{\lambda^2 - 0{\cdot}1253}; \quad \lambda_0^2 = 0{\cdot}1253,\ \lambda_0 = 0{\cdot}3562 \right\}$$

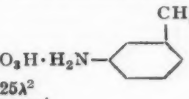
$$\left\{ [\alpha]^* = \frac{3{\cdot}367}{\lambda^2 - 0{\cdot}1269}; \quad \lambda_0^2 = 0{\cdot}1269,\ \lambda_0 = 0{\cdot}3540 \right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3300	1·3297	−0·0003	1·3301	+0·0001	−0·0004
Na_{5893} ..	1·3306	1·3309	+0·0003	1·3304	+0·0002	+0·0005
Hg_{5780} ..	1·3311	1·3311	±0·0000	1·3310	−0·0001	+0·0001
Hg_{5461} ..	1·3317	1·3320	+0·0003	1·3314	−0·0003	+0·0006
Hg_{4358} ..	1·3378	1·3377	−0·0001	1·3378	±0·0000	−0·0001

* The rotatory dispersion equation is taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, **6**, 15 ; *Allahabad University Studies*, 1944, **37**.

TABLE IV

Refractive Dispersion of m-*Toluidinocamphor-β-sulphonates*



$$\left\{n^2 = 1{\cdot}7511 + \frac{0{\cdot}01325\lambda^2}{\lambda^2 - 0{\cdot}1249};\right. \qquad \left.\begin{matrix}\lambda_0{}^2 = 0{\cdot}1249\\ \lambda_0 = 0{\cdot}3536\end{matrix}\right\}$$

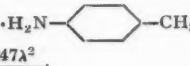
$$\left\{[\alpha]^* = \frac{3{\cdot}31}{\lambda^2 - 0{\cdot}1250};\right. \qquad \left.\begin{matrix}\lambda_0{}^2 = 0{\cdot}1250\\ \lambda_0 = 0{\cdot}3533\end{matrix}\right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3302	1·3304	+0·0002	1·3304	+0·0002	±0·0000
Na_{5893} ..	1·3311	1·3310	−0·0001	1·3312	+0·0001	−0·0002
Hg_{5780} ..	1·3313	1·3313	±0·0000	1·3314	+0·0001	−0·0001
Hg_{5461} ..	1·3319	1·3320	+0·0001	1·3320	+0·0001	±0·0000
Hg_{4358} ..	1·3378	1·3378	±0·0000	1·3374	−0·0004	+0·0004

* The rotatory dispersion equation is taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, **6**, 15 ; *Allahabad University Studies*, 1944, 37.

TABLE V

Refractive Dispersion of p-*Toluidinocamphor-β-sulphonates*



$$\left\{n^2 = 1{\cdot}7520 + \frac{0{\cdot}01247\lambda^2}{\lambda^2 - 0{\cdot}1276};\right. \qquad \left.\begin{matrix}\lambda_0{}^2 = 0{\cdot}1276\\ \lambda_0 = 0{\cdot}3597\end{matrix}\right\}$$

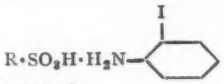
$$\left\{[\alpha]^* = \frac{3{\cdot}39}{\lambda^2 - 0{\cdot}1294};\right. \qquad \left.\begin{matrix}\lambda_0{}^2 = 0{\cdot}1294\\ \lambda_0 = 0{\cdot}3571\end{matrix}\right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3302	1·3303	+0·0001	1·3302	±0·0000	+0·0001
Na_{5893} ..	1·3310	1·3309	−0·0001	1·3311	+0·0001	−0·0002
Hg_{5780} ..	1·3311	1·3311	±0·0000	1·3312	+0·0001	−0·0001
Hg_{5461} ..	1·3318	1·3318	±0·0000	1·3316	−0·0002	+0·0002
Hg_{4358} ..	1·3379	1·3379	±0·0000	1·3380	+0·0001	−0·0001

* The rotatory dispersion equation is taken from Singh, B. K., Perti, O. N., and Singh, B. N., *Proc. Lahore Phil. Soc.*, 1944, **6**, 15 ; *Allahabad University Studies*, 1944, 37.

TABLE VI

Refractive Dispersion of o-*Iodanilinocamphor-β-sulphonates*



$$\left\{ n^2 = 1{\cdot}7632 + \frac{0{\cdot}00865\lambda^2}{\lambda^2 - 0{\cdot}1339}; \qquad \begin{matrix} \lambda_0{}^2 = 0{\cdot}1339 \\ \lambda_0 = 0{\cdot}3669 \end{matrix} \right\}$$

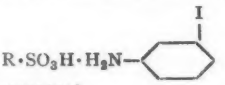
$$\left\{ [\alpha]^* = \frac{3{\cdot}11}{\lambda^2 - 0{\cdot}1346}; \qquad \begin{matrix} \lambda_0{}^2 = 0{\cdot}1346 \\ \lambda_0 = 0{\cdot}3659 \end{matrix} \right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3325	1·3328	+0·0003	1·3324	−0·0001	+0·0004
Na_{5893} ..	1·3331	1·3330	−0·0001	1·3330	−0·0001	±0·0000
Hg_{5780} ..	1·3332	1·3331	−0·0001	1·3333	+0·0001	−0·0002
Hg_{5461} ..	1·3337	1·3335	−0·0002	1·3340	+0·0003	−0·0005
Hg_{4358} ..	1·3388	1·3390	+0·0002	1·3389	+0·0001	+0·0001

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, **29**, 107.

TABLE VII

Refractive Dispersion of m-*Iodanilinocamphor-β-sulphonates*



$$\left\{ n^2 = 1{\cdot}7648 + \frac{0{\cdot}008138\lambda^2}{\lambda^2 - 0{\cdot}1345}; \qquad \begin{matrix} \lambda_0{}^2 = 0{\cdot}1345 \\ \lambda_0 = 0{\cdot}3664 \end{matrix} \right\}$$

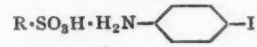
$$\left\{ [\alpha]^* = \frac{3{\cdot}268}{\lambda^2 - 0{\cdot}1342}; \qquad \begin{matrix} \lambda_0{}^2 = 0{\cdot}1342 \\ \lambda_0 = 0{\cdot}3667 \end{matrix} \right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3328	1·3328	±0·0000	1·3327	−0·0001	+0·0001
Na_{5893} ..	1·3335	1·3334	−0·0001	1·3332	−0·0003	+0·0002
Hg_{5780} ..	1·3336	1·3337	+0·0001	1·3334	−0·0002	+0·0003
Hg_{5461} :	1·3340	1·3338	−0·0002	1·3341	+0·0001	−0·0003
Hg_{4358} ..	1·3389	1·3388	−0·0001	1·3390	+0·0001	−0·0002

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. cad. Sci.*, 1949, **29**, 107.

TABLE VIII

Refractive Dispersion of p-*Iodanilinocamphor-β-sulphonates*



$$\left\{n^2 = 1{\cdot}7644 + \frac{0{\cdot}008404\lambda^2}{\lambda^2 - 0{\cdot}1333};\quad \lambda_0{}^2 = 0{\cdot}1333,\ \lambda_0 = 0{\cdot}3658\right\}$$

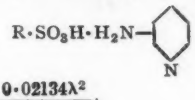
$$\left\{[\alpha]^* = \frac{3{\cdot}207}{\lambda^2 - 0{\cdot}1338};\quad \lambda_0{}^2 = 0{\cdot}1338,\ \lambda_0 = 0{\cdot}3637\right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3328	1·3327	−0·0001	1·3328	±0·0000	−0·0001
Na_{5893} ..	1·3334	1·3333	−0·0001	1·3335	+0·0001	−0·0002
Hg_{5780} ..	1·3336	1·3338	+0·0002	1·3337	+0·0001	+0·0001
Hg_{5461} ..	1·3340	1·3341	+0·0001	1·3339	−0·0001	+0·0002
Hg_{4358} ..	1·3389	1·3390	+0·0001	1·3387	−0·0002	+0·0003

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1949, **29**, 107.

TABLE IX

Refractive Dispersion of α-Aminopyridinocamphor-β-sulphonates



$$\left\{n^2 = 1{\cdot}7432 + \frac{0{\cdot}02134\lambda^2}{\lambda^2 - 0{\cdot}1084};\quad \lambda_0{}^2 = 0{\cdot}1084,\ \lambda_0 = 0{\cdot}3289\right\}$$

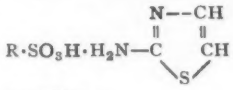
$$\left\{[\alpha]^* = \frac{4{\cdot}367}{\lambda^2 - {\cdot}1082};\quad \lambda_0{}^2 = 0{\cdot}1082,\ \lambda_0 = 0{\cdot}3292\right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3309	1·3310	+0·0001	1·3310	+0·0001	±0·0000
Na_{5893} ..	1·3320	1·3321	+0·0001	1·3319	−0·0001	+0·0002
Hg_{5780} ..	1·3321	1·3321	±0·0000	1·3322	+0·0001	−0·0001
Hg_{5461} ..	1·3329	1·3328	−0·0001	1·3331	+0·0002	−0·0003
Hg_{4358} ..	1·3390	1·3390	±0·0000	1·3389	−0·0001	+0·0001

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1947, **26**, 61.

TABLE X

Refractive Dispersion of α-Aminothiazolecamphor-β-sulphonates



$$\left\{ n^2 = 1{\cdot}7535 + \frac{0{\cdot}01311\lambda^2}{\lambda^2 - 0{\cdot}1256}; \quad \lambda_0^2 = 0{\cdot}1256,\ \lambda_0 = 0{\cdot}3537 \right\}$$

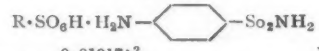
$$\left\{ [\alpha]^* = \frac{4{\cdot}155}{\lambda^2 - 0{\cdot}1251}; \quad \lambda_0^2 = 0{\cdot}1251,\ \lambda_0 = 0{\cdot}3544 \right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3310	1·3312	+0·0002	1·3311	+0·0001	+0·0001
Na_{5893} ..	1·3319	1·3318	−0·0001	1·3320	+0·0001	−0·0002
Hg_{5780} ..	1·3321	1·3321	±0·0000	1·3320	−0·0001	+0·0001
Hg_{5461} ..	1·3327	1·3330	+0·0003	1·3329	+0·0002	+0·0001
Hg_{4358} ..	1·3387	1·3387	±0·0000	1.3384	−0·0003	+0·0003

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1947, **26**, 61.

TABLE XI

Refractive Dispersion of p-*Aminobenzene Sulphonamidocamphor-β-sulphonates*



$$\left\{ n^2 = 1{\cdot}7575 + \frac{0{\cdot}01017\lambda^2}{\lambda^2 - 0{\cdot}1351}; \quad \lambda_0^2 = 0{\cdot}1351,\ \lambda_0 = 0{\cdot}3668 \right\}$$

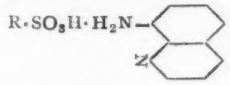
$$\left\{ [\alpha]^* = \frac{2{\cdot}793}{\lambda^2 - 0{\cdot}1346}; \quad \lambda_0^2 = 0{\cdot}1346,\ \lambda_0 = 0{\cdot}3676 \right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}	n_{d-r}
Li_{6708} ..	1·3312	1·3314	+0·0002	1·3314	+0·0002	±0·0000
Na_{5893} ..	1·3320	1·3321	+0·0001	1·3320	±0·0000	+0·0001
Hg_{5780}	1·3321	1·3321	±0·0000	1·3322	+0·0001	−0·0001
Hg_{5461} ..	1·3327	1·3329	+0·0002	1·3328	+0·0001	+0·0001
Hg_{4358} ..	1·3389	1·3387	−0·0002	1·3387	−0·0002	±0·0000

* The rotatory dispersion equation is taken from Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, 1945, **22**, 84.

TABLE XII

Refractive Dispersion of 6-Methoxy-8-aminoquinolinocamphor-β-sulphonates



$$\left\{n^2 = 1{\cdot}7315 + \frac{0{\cdot}03158\lambda^2}{\lambda^2 - 0{\cdot}1006};\right. \qquad \left.\begin{matrix}\lambda_0{}^2 = 0{\cdot}1006\\ \lambda_0 = 0{\cdot}3131\end{matrix}\right\}$$

$$\left\{[\alpha]^* = \frac{3{\cdot}294}{\lambda^2 - 0{\cdot}3098};\right. \qquad \left.\begin{matrix}\lambda_0{}^2 = 0{\cdot}098\\ \lambda_0 = 0{\cdot}3172\end{matrix}\right\}$$

λ	$n_{\text{Calculated}}$ (c)	n_{Laevo} (l)	n_{l-c}	n_{Dextro} (d)	n_{d-c}	n_{Racemic} (r)	n_{r-c}
Li_{6708} ..	1·3312	1·3312	±0·0000	1·3310	−0·0002	1·3311	−0·0001
Na_{5893} ..	1·3327	1·3328	+0·0001	1·3327	±0·0000	1·3328	+0·0001
Hg_{5780} ..	1·3329	1·3329	±0·0000	1·3329	±0·0000	1·3330	+0·0001
Hg_{5461} ..	1·3338	1·3337	−0·0001	1·3338	±0·0000	1·3336	−0·0002
Hg_{4358} ..	..	..	..	..	..	..	..

* The rotatory dispersion equation is taken from Singh, B. K., and Manhas, K. M. S., *Proc. Ind. Acad. Sci.*, 1947, **26**, 61.

"Characteristic" absorption bands—have been calculated from these equations and are compared with those derived from rotatory dispersion equations of Drude and are found to be in fairly close agreement (Table I). The equations of rotatory dispersion for these eleven salts[5] are reproduced in Tables II–XII for the sake of comparison.

THE EFFECT OF CONSTITUTION ON THE "CHARACTERISTIC" ABSORPTION BAND IN THE ULTRA-VIOLET REGION

The wavelength of the "Characteristic" absorption band of anilinocamphor-β-sulphonates is 3613 A°.U. The replacement of an hydrogen atom by a methyl group in the corresponding toluidino salts has shifted this band further to the ultraviolet end of the spectrum and the order of this shift in different position isomerides is as follows (Table I, Nos. 1, 2, 3, 4):

$$m > o > p > un.$$

If the substituent group is iodine, the shift of the "Characteristic" absorption band is towards the red end of the spectrum and the order is as follows (Table I, Nos. 1, 5, 6, 7):

$$m > o > p > un.$$

The substitution of the pyridine ring for the benzene nucleus (Table I, Nos. 1 and 8) produces a shift of about 323 A°.U. in the wavelength of the "Characteristic" absorption band towards the ultraviolet side, whereas the thiazole ring (Table I, Nos. 1 and 9) produces a similar but much smaller shift (about 73 A°.U.). The substitution of the sulphonamido group in the para position for an hydrogen atom in the benzene nucleus (Table I, Nos. 1 and 10) produces, however, a small shift of about 59 A°.U. to the red end of the spectrum. The substitution of 6-methoxyquinoline ring for the phenyl group produces a remarkably large shift of about 462 A°.U. of the "Characteristic" absorption band towards the ultraviolet end of the spectrum (Table I, Nos. 1 and 11).

The effects of dispersion can be eliminated from both the Drude as well as the Maxwell-Sellmeier equations by making $\lambda^2 - \lambda_0^2 = 1$; in the case of the Drude equation the value of rotatory power becomes equal in magnitude to that of k_0, the rotation constant. The value of refractive index, n_{abs}, in the Maxwell-Sellmeier equation for the corresponding wavelength λ, where $\lambda^2 = 1 + \lambda_0^2$, may be taken as the absolute measure of the refractive index of the medium in which the effect of wavelength, *i.e.*, dispersion, is eliminated as in the case of the values of $k_0 s$.

A comparison of $k_0 s$ with n_{abs} or $\sqrt{a^2 + b_0 (1 + \lambda_0^2)}$, however, reveals no simple relationship: in the case of toluidino camphor-β-sulphonates when k_0 decreases, the corresponding values of n_{abs} also decrease. On the other hand in the case of iodanilino salts the result is opposite.

The nature of the Racemic Forms of the Camphor-β-Sulphonates

A glance at Tables II-XII reveals that the refractive indices of the dextro and the racemic forms in the visible spectrum for 5 wavelengths (λ_{6708} to λ_{4358}) are identical in 1% (or less) aqueous solution within the limits of experimental error. In the absence of any differences in the values of refractive indices of the two forms in dilute solutions, it is not possible to draw any unequivocal conclusion regarding the nature of the racemic modification.

The Rotatory and Refractive Dispersion Studies as an Aid in the Determination of the Characteristic Ultraviolet Absorption Bands; Analogy with Raman Spectra in the Infra-red Region

We have seen that our studies of refractive and rotatory dispersion, using the Maxwell-Sellmeier and the Drude equations respectively, give us

almost identical values of $\lambda_0 s$—the wavelengths of the dominant absorption bands of the molecules in the ultraviolet region of the spectrum (Table I). We have not verified these bands by direct measurements in the present work but in Part I of this series[1], the values of the dominant absorption bands for camphor in the ultraviolet region obtained from dispersion data were found to agree with those determined by direct absorption measurements. The utility of rotatory and refractive dispersion studies is thus evident: it has brought the study of the ultraviolet absorption spectra within the region of the visible spectrum technique. The case is, therefore, analogous to the Raman spectra which has enabled the determination of the position of the infra-red absorption bands of molecules by measurements in the visible region.

Experimental

The compounds described in this paper were prepared and purified by methods described elsewhere.[5]

The refractive indices were determined with a Pulfrich Refractometer: water maintained at 33–35° C. was circulated through the jacketed mount of the observation cell containing the solution. The concentration of the aqueous solutions of the salts was 1% (namely, 1·0 gram in 100 c.c. of the solution) except in the case of *o*-, *m*- and *p*-iodanilinocamphor-β-sulphonates for which 0·5% solution were used. The experimental results are given in Tables II–XII.

Summary

1. The refractive dispersion of salts of camphor-β-sulphonic acid (*d*- and *dl*-) with eleven primary aromatic and heterocyclic bases was determined in aqueous solution for five wavelengths (λ_{6708} to λ_{4358}). The results can be accurately represented by the Maxwell-Sellmeier equation, using only one term of the summation.

2. It is found that the values of the wavelengths of the " Characteristic " absorption bands ($\lambda_0 s$) deduced from the present measurements on refractive dispersion of these salts are almost identical with those deduced from the rotatory dispersion measurements previously described.

3. The effect of replacement of an hydrogen atom of the phenyl group in anilinocamphor-β-sulphonate by different groups has been discussed.

4. The values of the refractive dispersion of the dextro and the racemic salts are identical in dilute solution.

5. The utility of the dispersion studies for the determination of the dominant absorption bands of the molecules in the ultraviolet region has

been stressed and its analogy with Raman spectra for infra-red absorption bands pointed out.

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